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FINAL REPORT

PROJECT NO. A-446-2

KINETICS OF THE REACTIONS INVOLVED IN THE FERRIC CHLORIDE ETCHING OF COPPER PHOTOENGRAVING PLATES

By

W. H. BURROWS, C. T. LEWIS, JR.,
and
D. E. SAIRE

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ABSTRACT

Experimental data show the heterogeneous reaction rate of copper with ferric chloride follows a second order polynomial dependency on the solution molarity for 25°, 35° and 45° C over a flow rate range of 700 to 5500 milliliters per minute. A slight fourth order dependence exists at 45° C. All trials exhibited maximum dissolution around 2.15-molar ferric chloride. Temperature coefficients, Arrhenius activation energies, reaction rate, flow rate dependence and sample position dependence of the reaction rate all support the proposition that the reaction is diffusion-controlled. Dissolved oxygen in the ferric chloride inhibits the reaction and is thought to be a surface poison. Viscosity and density data used with a derived equation show the reactivity of the species in increasing order to be Fe^{+3} and $FeOH^{+2}$, $FeCl_2^+$ and $FeCl^{+2}$. $FeCl_3$ is not believed to be reactive.

Inhibitor studies were conducted to investigate thiourea, ethylene thiourea and formamidine disulfide. Several maxima and minima in the dissolution-rate-versus-inhibitor-concentration curve were observed with a rather sharp decrease in reaction rate occurring at 2.5×10^{-3} gram moles per liter of inhibitor. Temperature and flow rate effects on the inhibiting effects of formamidine disulfide were observed.

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I. INTRODUCTION

Heterogeneous chemical reactions are usually classified as complex, since the reactions are governed not only by chemical effects, but also by physical phenomena occurring at the interface. These interfacial effects influence the overall rate of reaction and where the chemical reaction rate is sufficiently high become the controlling mechanism. Rates of complex reactions depend upon the concentrations of the reactants and of any intermediate products formed during the reaction.

In complex reactions of the heterogeneous type, consisting of a solid phase and a liquid phase, the reacting species must diffuse through the solvent to the solid surface before the chemical reaction may occur. In most cases the reacting species is adsorbed on the surface of the solid and held by either polar bonds or attractive forces of other than chemical nature. This adsorbed species is the reaction intermediate with which the solid surface reacts. The reaction products must then diffuse from the surface into the solution. There are therefore three distinct steps that must occur for the reaction to be complete:

1. Transport of the reactant species to the interface by convection and diffusion.
2. Chemical reaction on the surface.
3. Transport of the reaction products from the surface into the solution.

The slowest of these becomes the rate-controlling step.

Nernst (1) postulated a general heterogeneous reaction theory which described the reaction as occurring quite rapidly at the solid-liquid interface, thereby depleting the reacting species in the liquid nearby. The depletion of the reactants near the interface then makes the controlling mechanism one of

diffusion of the active species through a boundary layer in order to react at the surface. The reaction velocity is, therefore, slower than the chemical reaction rate and should be equal to the diffusion velocity of the reactants. Van Name and Hill (2) concluded that, if this is correct, all metals should dissolve at the same rate in the same reagents at identical conditions of concentrations, temperature and other variables. However, some of their work contradicted this postulate and they proposed three possible types of heterogeneous reaction controls. The first agreed with the theory of Nernst, in that the diffusion of the active species to the interface was the controlling mechanism. Certain of the reactions studied by Van Name and Hill were controlled by the chemical reaction rate at the surface, while others appeared to be controlled by both the diffusion and chemical mechanisms.

C. V. King (3) postulated a general theory of diffusion-controlled reactions consisting of five criteria. These were expanded by Salzberg, Knoetgen and Molless (4) to their final form:

1. Different metals dissolve at nearly the same rate in the same reagent under identical conditions of temperature, agitation, etc.

2. The rate of agitation of the solution past the metal surface has a great effect. The greater the agitation, the greater is the dissolution rate.

3. The dissolution rates as determined with a series of reagents of varying concentration are proportional to a fractional power of the diffusion coefficients, about 0.75.

4. The dissolution rate is approximately inversely proportional to the viscosity.

5. The dissolution rate increases with increasing concentration of reagent, the curve being linear.

6. The temperature coefficients of diffusion-controlled reactions are lower than for homogeneous reactions or chemical-controlled reactions, usually between 1.1 and 1.5 per 10° C rise in temperature.

(7) The previous condition of the surface has only a very minor effect on the dissolution rate.

(8) All crystallographic orientations of the metal dissolve at the same rate.

(9) Diffusion-controlled rates are generally higher than chemical-controlled rates in solutions with similar physical properties.

Salzburg et al proposed large standard oxidation-reduction potentials for diffusion-controlled reactions and indicated that reactions having small oxidation-reduction potentials would be chemically controlled. The limiting case of ferric ion-silver reaction was suggested to be controlled by diffusion, whereas the reaction couples of smaller potentials would be chemically controlled. However, this division is only general and contradictions to it have been observed. Ferric ion-copper system, by this criterion, should be diffusion-controlled.

Chemical-controlled reactions have criteria opposed to those postulated for diffusion-controlled reactions. The reaction rate increases nonlinearly with increasing reagent concentration and reaches a maximum. As Van Name and Hill (2) noted, controlling mechanisms exist which lie between pure diffusion control and pure chemical control. Their results on the system copper-ferric alum solutions showed the reaction as not entirely diffusion-controlled. Other investigations (5, 6, 7, 8, 9) have shown systems having both chemical and diffusion control combined.

Benjamin, Lu and Graydon (10) proposed that the reaction rate of the sulfuric acid dissolution of copper was controlled by the rate of oxidation of the cuprous ion at the interface. Kuzminykh et al (11), investigating the same reaction, concluded that the reaction rate was only slightly dependent on the sulfuric acid concentration. Temperature coefficients for the system between

20° and 60° C varied from 1.3 to 1.5 per 10° C rise. This would indicate a diffusion-controlled reaction. However, for temperatures above 60° C temperature coefficients were reported in excess of two. Thus a diffusion-controlled mechanism operates at low temperatures and is replaced by chemical control at high temperatures.

The copper-nitric acid reaction has been investigated by Milyutin and Shutlin over a wide range of concentrations (12). At moderate concentrations the reaction was found to be controlled by the chemical reaction rate at the surface, while at nitric acid concentrations greater than 11.0 molar the diffusion of the active species became the controlling mechanism. The type of controlling mechanism was indicated by temperature coefficient criteria. Johnson, Hobson and Weber (13) later confirmed this observation.

The work of Weeks and Hill (14), using an alloy containing radioactive cobalt to follow the dissolution rate of copper in sulfuric acid, showed the reaction to be chemically controlled. However the phase diagram for copper-cobalt alloys excludes any alloys of other than a very low cobalt concentration and the homogeneity of the sample is in question. The reported accuracy limits of 20 per cent tend to support the lack of a homogeneous sample.

King and Weidenhammer (15) performed the first experiments on the system ferric chloride-copper. They reported copper dissolving much slower than magnesium, zinc, or cadmium under the same conditions. Low temperature coefficients and an approximately inverse proportionality between the solution viscosity and the reaction rate led to the conclusion of a diffusion-controlled mechanism for the copper-ferric chloride system. Pletenev and Pavlov (16), in their investigation of the same system at concentrations less than 0.4-molar ferric chloride, reported a linear relation between the reaction rate and the

concentration. At higher concentrations the reaction rate did not increase linearly with ferric chloride molarity. Upon coating the copper surface with gelatin and observing a large decrease in the reaction rate, the authors concluded that the reaction was diffusion-controlled.

Szabo (17), observing no dependence of the reaction rate on the rate of stirring, concluded that the copper-ferric chloride reaction is chemically controlled.

Brooks (18) and Ferrari (19) investigated the reaction between copper and ferric chloride solutions up to a concentration of 3.33-molar ferric chloride. Their work showed increasing reaction rate with increasing concentration, a maximum at 2.25 molar, and a continual decrease with further increase of ferric chloride concentration. It was postulated that the controlling mechanism was one of diffusion of the active species to the copper surface. Brooks further proposed the active species to be Fe^{+3}, $FeCl^{+2}$, and $FeCl_2^{+}$.

This report summarizes the work performed from April 1, 1959, to March 31, 1961. The purpose of this work was to investigate completely the mechanisms involved in the reaction of copper with ferric chloride solution using radioisotope tracer techniques. This included the investigation of such variables as temperature, ferric chloride concentration, dissolved gas content of the solution, linear flow rate, time of reaction, and various inhibitors added to the system.

Phase I, covering the period from April 1, 1959, to March 31, 1960, was directed toward obtaining accurate measurements of the reaction rates of copper with ferric chloride solutions under varying temperatures and concentrations. Kinetic runs were made at 25°, 35° and 45° C, with the ferric chloride solution

concentration varying from 0.5 to 3.5 molar. The isotope copper-64 was used as a tracer in measuring the dissolution rate of copper.

Phase II, covering the period from April 1, 1960, to March 31, 1961, was concerned with studying the effect of variables such as solution flow rate, time of reaction, and dissolved oxygen and nitrogen content of the solution. Extensive experiments were performed to investigate the inhibiting effect of ethylene thiourea, thiourea and formamidine disulfide. Also included were studies of the effects of temperature and solution flow rate at varying concentrations of these inhibitors. In the studies of inhibitors, radioactive sulfur was used to label these compounds for radioassay. In addition, calculations were made to determine the viscosity effect upon the mass transport of the reacting species to the metal surface and the effect of this factor upon the rate of the diffusion-controlled reaction.

The following personnel have served on this project during the period covered in the report:

Project Director: Mr. W. H. Burrows, Head, Industrial Products Branch

Consultant: Dr. Allan C. Topp, Faculty Research Associate

Research Assistant: Mr. C. Turner Lewis, Jr.

Graduate Research Assistant: Mr. Donald E. Saire

This project has served as thesis research in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering for Mr. Saire.

II. EXPERIMENTAL WORK

A. Equipment

All of the rate determinations in the investigation were performed in specially designed equipment. The apparatus consisted of a reaction cell, together with circulating equipment, reservoir, and a temperature-controlling system (see Figure 1). The reaction cell was mounted so that the ferric chloride solution rose vertically in it and encountered the copper sample mounted face down in a horizontal position. The lower portion of the cell contained a packing material to distribute the flow evenly over the entire cross-sectional area of the cell. A standard taper stopcock, modified by the addition of a flattened glass rod, served as the sample holder for the copper. The copper sample was a 1- x 3-cm piece that was cut from a 1/32-inch sheet of electrolytic copper. The back and sides of the copper sample were coated to prevent etching except on the front surface.

The ferric chloride solution flowed to the reaction cell from the solution reservoir, a three-neck round-bottom flask to which a small standard taper port had been added. The center neck held a thermometer, while the two side necks held the inlet and outlet tubes. The small standard taper port was used for withdrawing aliquots for assay. The reservoir was heated by a mantle powered through a calibrated voltage control, and flow through the entire system was sufficiently rapid that uniform temperature in the reaction cell was maintained by controlling the temperature in the reservoir. The experimental apparatus was connected by 3/8-inch-ID Tygon tubing, through which a Sigmamotor pump circulated the ferric chloride solution.

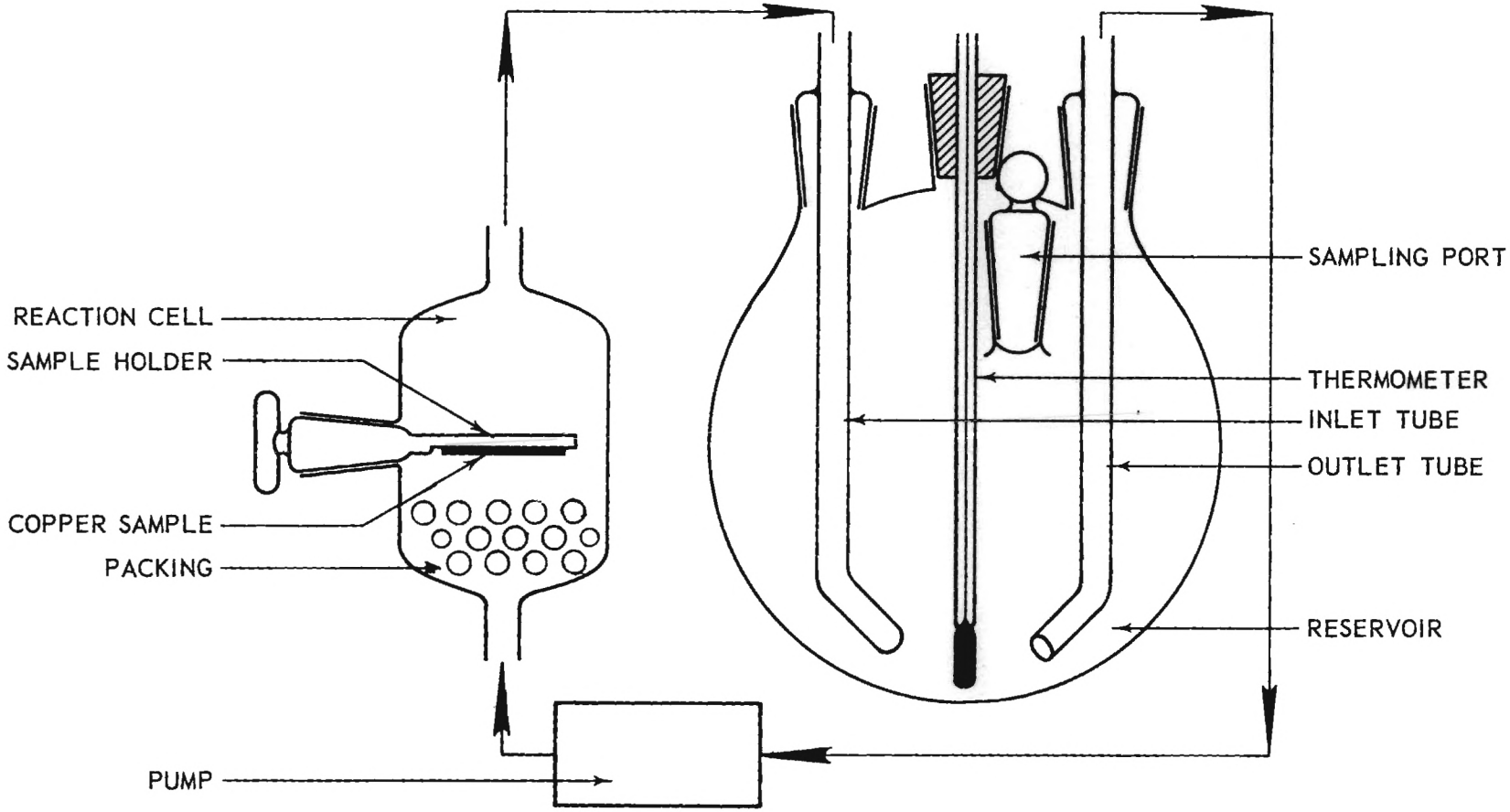

Figure 1. Reaction Cell and Accessories.

At the start of Phase II of the project it was felt that greater control of solution variables was needed. The flow rate through the Sigmamotor pump decreased during the runs and was constantly pulsating. To correct this situation a Jabsco neoprene-plastic pump with a titanium shaft was obtained and coupled to a Zero-Max variable speed drive. The variable speed drive afforded an excellent method of changing flow rates to study their effect on the copper dissolution rate.

To facilitate the investigation of the influence of dissolved oxygen on reaction rates, a gas dispersion unit was constructed and placed in the solution reservoir. In all runs concerned with dissolved oxygen, the oxygen was dispersed into the solution for a sufficient time before the start of a run to saturate the ferric chloride and during the run to act as a blanket gas.

Temperature control was changed from the heating mantle with variable voltage control to a glass heat exchanger through which the solution passed. A variable temperature water supply was passed through the shell side of the heat exchanger to regulate the ferric chloride solution temperature. Control of the reaction system temperature was held to within ±0.1° C.

B. Materials and Supplies

The experimental concentrations of ferric chloride used in this study were prepared by making a stock solution of approximately 4.0 molar. This solution was prepared by accurately weighing out a known amount of reagent grade ferric chloride and dissolving it in a measured volume of distilled water. The molarity of this solution was obtained by measuring its density at 20° C with a Westphal balance and determining the concentration from the data given in Lange's Handbook of Chemistry (20). An equation was fitted to these data

by the least squares method to permit direct conversion of density readings to ferric chloride molarity without extrapolation. The experimental concentrations were obtained from this stock solution by accurate dilution, and the concentrations of these diluted solutions were remeasured by the above-mentioned method.

Copper samples were made from electrolytic photoengraver's copper, 1/32-inch-thick. Spectrographical analysis showed traces of impurities of silver and chromium; however, the purity of the copper remained greater than 99.99 per cent. The samples were cut to a slight oversize of 1 x 3 cm, stacked, and reduced to precise dimensions on a surface-grinding machine. They were cleaned with a sodium-chloride-saturated 5 per cent hydrochloric acid solution, then accurately weighed to six significant figures. A coating of Krylon was applied to all surfaces except the reaction surface to guarantee no etching in undesired locations.

Sulfur-35-labeled thiourea was purchased for the inhibitor studies. The conversion of this thiourea into the dihydrochloride of formamidine disulfide had many troublesome steps. In the current method of preparation, as the reaction product of thiourea and ferric chloride, the thiourea was dissolved steadily into 2.15-molar ferric chloride at room temperature. Evolution of heat, accompanied by several color changes, preceded precipitation of the reaction product. Removal of all moisture and traces of ferric chloride was mandatory to prevent subsequent degradation of the formamidine disulfide in any solvent system. Washing of the precipitate with isopropanol has been found to yield the highest quality crystals with the smallest degree of degradation (21).

C. Procedure

The Phase I experimental technique for determining the amount of copper in solution involved the development of a plating, drying, and counting

technique. Small quantities of phosphorus-32 and copper-64, as the nitrate, were used for this purpose prior to the actual experimental work. Experiments on sampling, plating, drying, and counting were performed with predetermined concentrations of these isotopes in ferric chloride solutions. These experiments were continued until the investigators had developed the technique to the point that successive samples and platings produced only small deviations that did not seem to contribute any appreciable experimental error.

With the plating and counting techniques well in hand, work was started on the actual kinetic runs using the uniform copper samples previously described. At periodic intervals, four copper samples and four control samples were forwarded to Oak Ridge to be irradiated in the ORNL graphite reactor. The control copper samples were accurately weighed on an analytical balance before the shipment was sent to Oak Ridge and thus served as a means of determining the level of activity of the irradiated copper and the amount of copper in the solution. This was accomplished by dissolving the control samples in aqua regia and placing 0.1 ml of this solution into 5 ml of the experimental ferric chloride concentration. From this solution, 0.1 ml was withdrawn, plated, dried, and counted on the same instruments used to count the activity of the experimental samples. The activity of this control solution was then converted to a counts-per-minute-per-gram factor that depended on the actual weight of the original control sample. This factor was used to convert the activity of the experimental sample in counts per minute, to grams of dissolved copper in solution. By making use of this control sample technique, possible counting errors that develop from geometry, backscatter, absorption and self-absorption were eliminated.

A group of experimental runs was performed whenever a shipment of irradiated copper was received from Oak Ridge. The reservoir was charged with ferric chloride solution, which was circulated through the system until a steady temperature reading was obtained. The copper samples were mounted on the sample holder with Pliobond adhesive and inserted in the reaction cell. The kinetic runs lasted for a period of 60 minutes, during which time samples were withdrawn from the reservoir with 0.1-ml pipettes every 6 minutes. Three samples were withdrawn at each sample period making a total of 30 samples for each experimental run. After being withdrawn from the solution reservoir, the samples were discharged into the center of 5-cm watch glasses and evaporated to dryness. The watch glasses containing the samples were placed on aluminum rings over the hot plates, which were regulated to a point where they would supply enough heat to warm the watch glasses. Overhead heat for evaporation was provided by infrared lamps mounted over hot plates. Careful control was maintained during the drying cycles in order to obtain deposits of uniform size and distribution. Once dried, the samples were stored in a desiccator until counted with a Geiger-Muller counting tube.

Data obtained from these runs were in terms of count rates that indicated the concentration of copper-64 ions present in the solution. The IBM 650 computer was used to convert these data into grams of copper dissolved, to calculate the per cent deviation for each time interval determination, and to apply least squares methods to determine the slope of the straight-line dissolution curve that gives the value of the rate constant for each run. To accomplish this a computer program (Figure 2) was written that converted counts per minute to grams of copper dissolved in the following stepwise procedure:

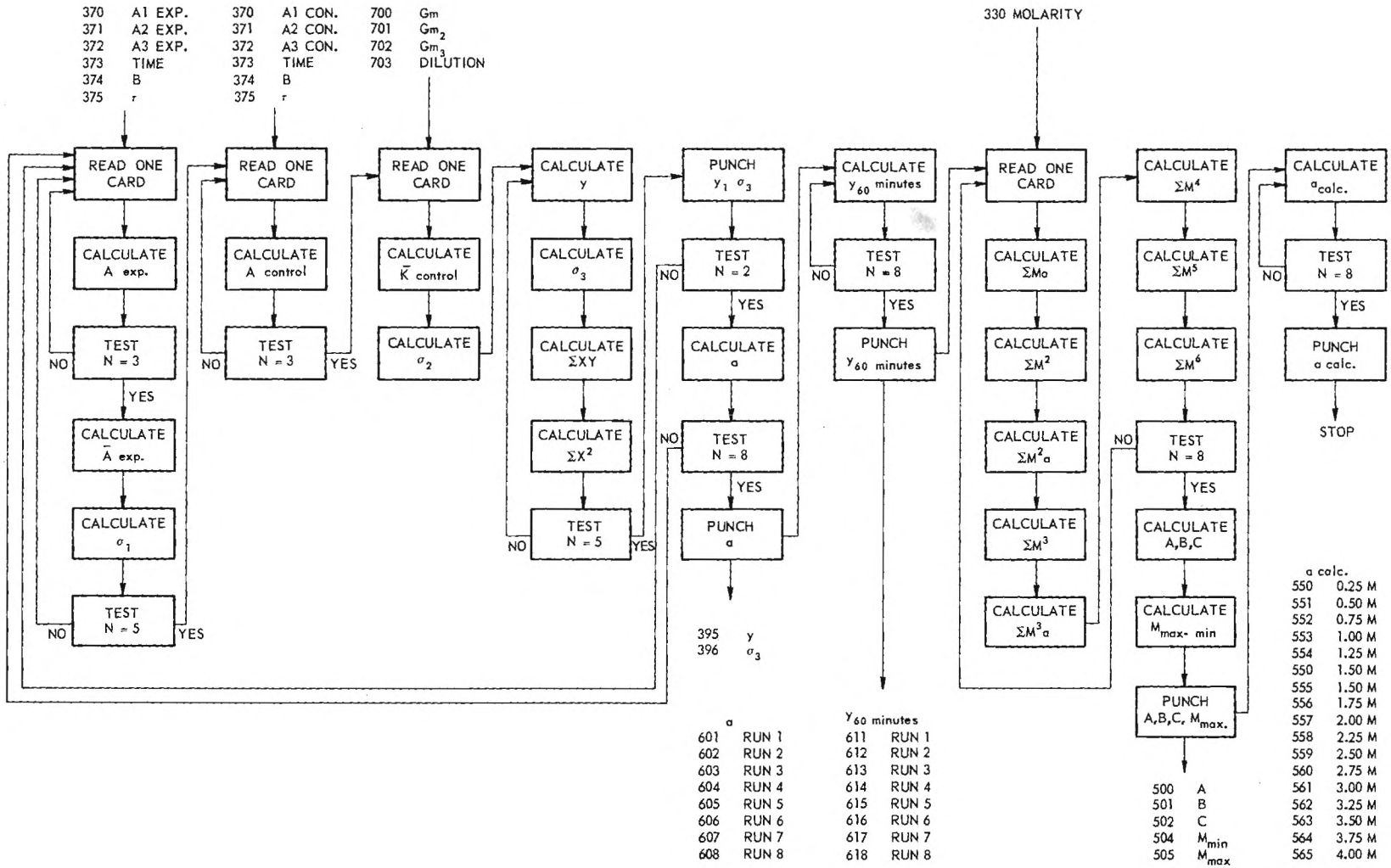

Figure 2. Outline of Computer Program.

(1) applied counting tube dead time correction factor to experimental data,

(2) subtracted background reading of counters from the data,

(3) made copper-64 half-life corrections,

(4) calculated the average counts per minute for the three experimental samples,

(5) calculated per cent deviation from the above average,

(6) calculated the grams of copper dissolved per sample from the average counts per minute and control sample factor, and

(7) performed least square fits of the data to yield calculated curves.

During Phase II of the project, the ferric chloride solution and associated equipment were brought to equilibrium at the desired temperature and flow rate at the start of each run. If a gas was to be dispersed in the etching solution, this was accomplished during the approximately 30 minutes required to reach temperature and flow rate equilibrium. A retarding of the etch rate due to a protective coating of the copper sample was eliminated by stopping the dispersion unit long enough before the start of the run to allow all the fine bubbles to be removed. The run was conducted under a blanket of the desired gas.

The mounted copper sample was then introduced into the reaction cell and the reaction allowed to run for up to 30 minutes. Upon removal, the sample was washed in acetone, dried, and weighed. From this loss in weight, the etch rate under the conditions of the experiment could be calculated. Any film studies or species studies could be followed simultaneously by use of radioactive tracers.

III. RESULTS AND DISCUSSION

A. Effects of Temperature and Concentration

Phase I of this study investigated the kinetics of the reaction between copper and ferric chloride as affected by varying the ferric chloride concentration and temperature. The reaction was studied at 25°, 35°, and 45° C with ferric chloride solutions ranging from 0.5 to 3.5 molar. Eight experiments were conducted at each temperature making a total of 24 completed runs. All experiments were run at a solution flow rate of 1450 milliliters per minute.

The data from each run in the form of counts per minute were converted by the previously described IBM 650 computer program into milligrams of copper dissolved versus the time of reaction. Since the reaction concentrations and volumes were chosen to insure a pseudo-zero-order reaction, the converted data could then be fitted by the computer to a straight line by the least squares method. The slope of this line is the rate of reaction, called hereafter the dissolution or etch rate. These data are presented in Table I. A plot of the dissolution rate versus ferric chloride molarity at each temperature showing the dependence of the reaction rate on the molarity is given in Figure 3. These curves were drawn on the basis of a combined least squares polynomial fit and a "F" goodness of fit program. For temperatures of 25° and 35° C the "F" goodness of fit test showed the dissolution rate dependence on the molarity to be second order. The 45° C experiments also showed a second order molarity dependence, but in addition a small dependence on the fourth order term of the polynomial. In general it can be concluded that the reaction rate has second order dependence upon the ferric chloride molarity.

TABLE I

EFFECT OF TEMPERATURE ON THE REACTION RATE

Flow Rate = 1450 Ml/Min
Reaction Time = 60 Min

$FeCl_3$ Concentration (M)	Dissolution Rate (Mg/Cm^2-Min)		
	25° C	35° C	45° C
0.5	1.05	1.39	1.46
1.0	1.84	2.49	2.80
1.5	2.40	3.26	3.91
2.0	2.72	3.67	4.67
2.25	2.79	3.73	4.89
2.5	2.80	3.69	4.97
3.0	2.66	3.27	4.70
3.5	2.30	2.39	3.76

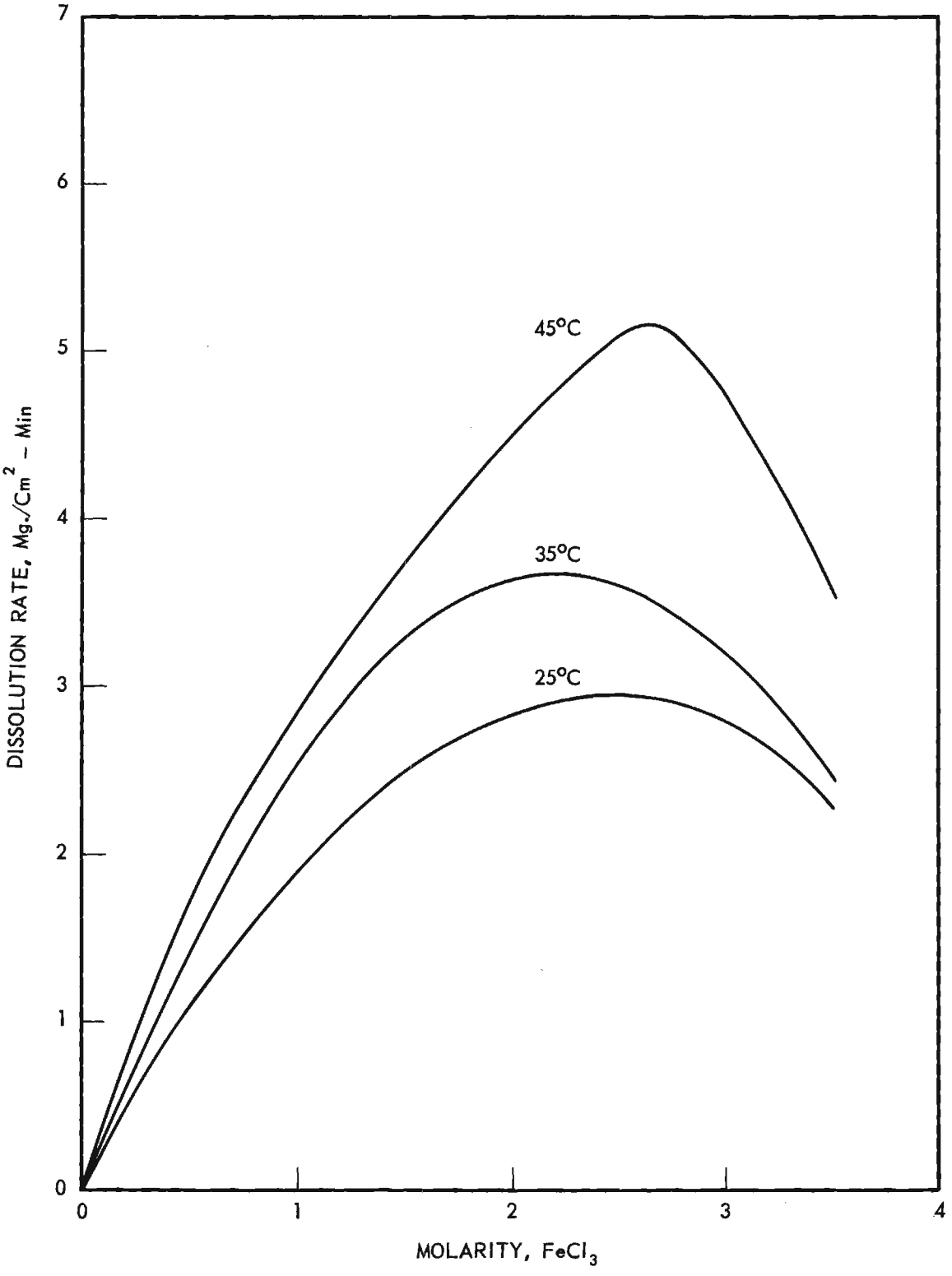

Figure 3. Dissolution Rate Dependency at Constant Temperatures.

Inspection of these curves shows that the dissolution rate curves increase linearly with respect to the ferric chloride molarity up to a concentration of about one molar. Above one molar the rate increases more slowly, reaching a maximum between a concentration of 2.0 and 2.5 molar and then decreasing with increasing molarity.

It is interesting to note that the dissolution rate curves are in general agreement with the data reported by Brooks (18) and Ferrari (19). Both of these investigators reported similar reaction rate curves with maximum values occurring between 2.0- and 2.5-molar ferric chloride. However, the work of these investigators was confined to temperatures at or below 25° C.

Calculated values of the temperature coefficients are presented in Table II. The coefficients $k_{45°}/k_{35°}$ and $k_{35°}/k_{25°}$ all lie between 1.04 and 1.57 per 10° C rise. From the general heterogeneous chemical reaction theory previously discussed this indicates the controlling mechanism to be one of diffusion control.

B. Activation Energies

Further indication that the reaction is controlled by a diffusion mechanism is given by the low energies of activation exhibited by the system. Abramson and King (22) have shown that activation energies in the range of 5,000 calories per mole are typical of diffusion-controlled reactions. By using the basic Arrhenius energy equation, activation energies for the copper-ferric chloride system at various molarities were calculated. The Arrhenius equation is represented as follows:

$$\ln\left(\frac{k_{t_2}}{k_{t_1}}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

TABLE II

TEMPERATURE COEFFICIENTS FOR THE REACTION OF COPPER IN FERRIC CHLORIDE SOLUTIONS

$FeCl_3$ Concentration (M)	$k_{35°}/k_{25°}$	$k_{45°}/k_{35°}$
0.5	1.32	1.05
1.0	1.35	1.12
1.5	1.36	1.20
2.0	1.35	1.27
2.25	1.34	1.31
2.5	1.32	1.35
3.0	1.23	1.44
3.5	1.04	1.57

where E_a is the activation energy for the reaction, k is the specific reaction velocity, R is the gas constant, and T is the absolute temperature.

Activation energies were obtained by plotting the logarithm of the reaction rate at constant molarity against the reciprocal of the absolute temperature. The slope of this line multiplied by the gas constant R (1.9872 calories per degree per mole) gives the value of the activation energy. A graph of the Arrhenius equation at various molarities is shown in Figure 4. Six calculated values of the activation energy range from 3810 to 4240 calories per mole. The average value was 4040 calories per mole. This compares to an average value of 4388 calories per mole for Ferrari (19), 1107 calories per mole for Brooks (18)

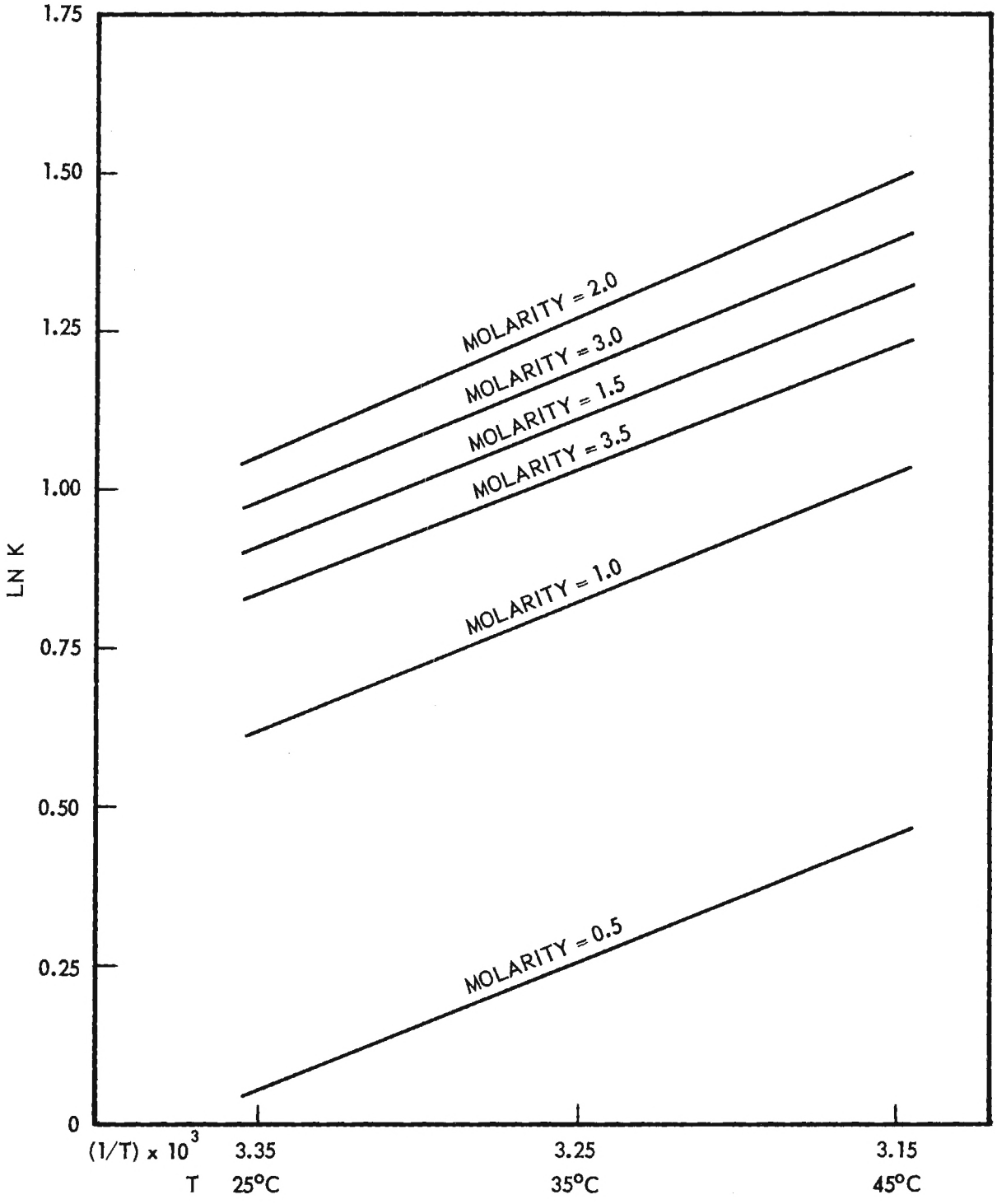

Figure 4. Arrehenius Energy Plots.

and 4887 calories per mole for Saire (23). In view of the very limited data of Brooks and the relatively close agreement of the remaining investigators it is felt that the determined values of this report are reliable. The average activation energy upholds the postulate of diffusion control.

C. Effects of Rate and Direction of Flow

Experimental runs conducted at 25° C under a nitrogen blanket are reported in Table III for flow rates of 700, 1400, 2100, and 5500 milliliters per minute. The results of these 44 runs are graphically represented by Figure 5. These are least squares fitted curves from the IBM-650 program for polynomials through fourth order. The goodness of fit test indicated that the curves are of second order dependence. Maximum etch rates occur around 2.15-molar ferric chloride.

Ferrari (19) obtained a linear dependency of the etch rate on the solution flow rate. His work was for reactions in which the surface of the copper was parallel to the direction of flow. A plot (Figure 6) of the dissolution rate found in this investigation, for flow perpendicular to the reaction surface, also reveals a linear dependence of the reaction rate at constant molarity on the solution flow rate. Extrapolation of the etch rate to zero solution velocity yields rates of 1.20, 2.31, and 2.02 milligrams per square centimeter per minute for molarities of 1.00, 2.15 and 3.00. These compare to Ferrari's values of 1.05, 2.38 and 1.94 milligrams per square centimeter per minute. That the slopes of the three curves have approximately the same value indicates a uniform effect of flow rate over the entire molarity range studied. The average value of this slope is 4.45×10^{-4} milligrams per square centimeter per milliliter.

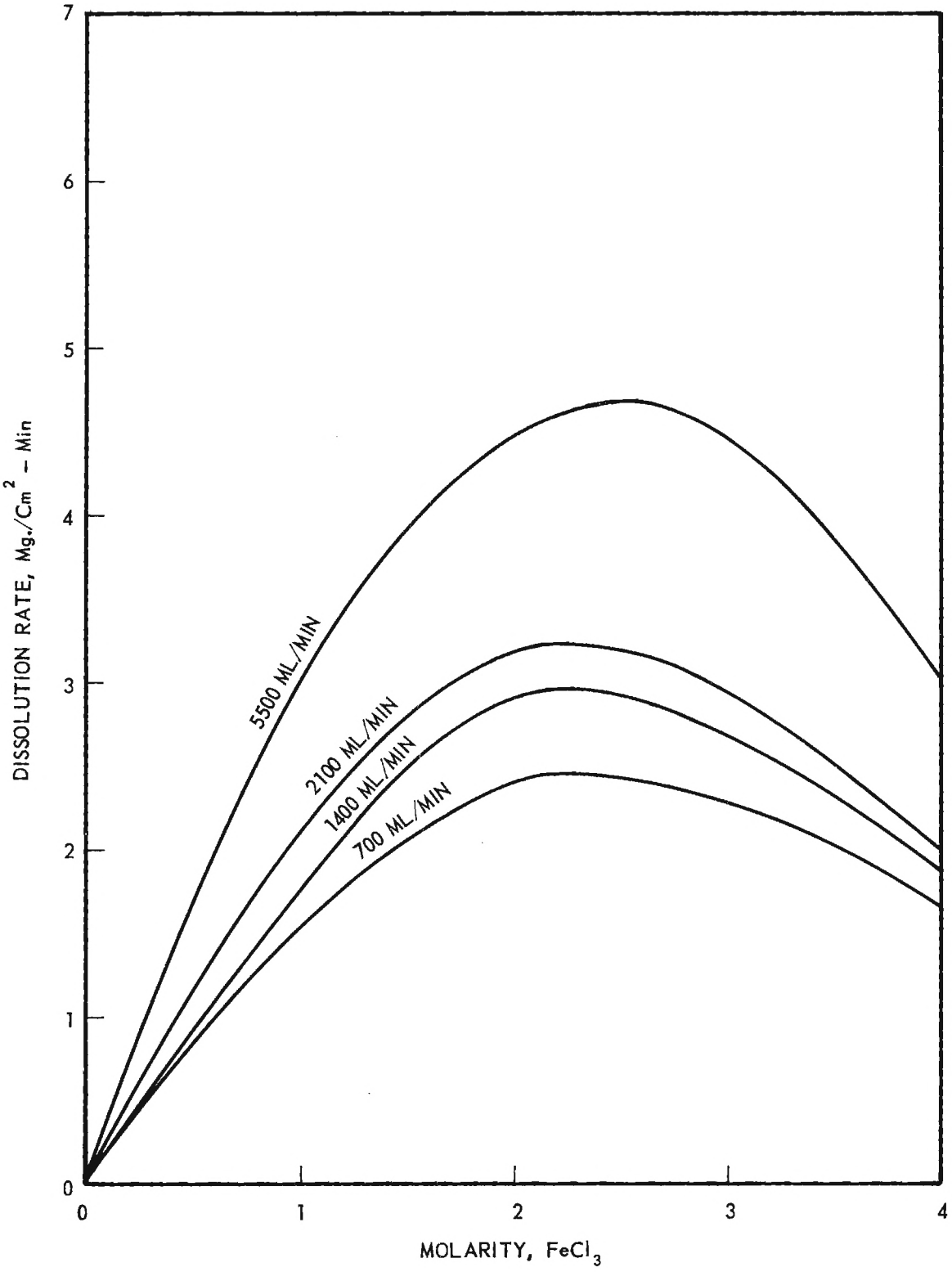

Figure 5. Dissolution Rate Dependency at Constant Flow Rates. Temperature = 25°C.

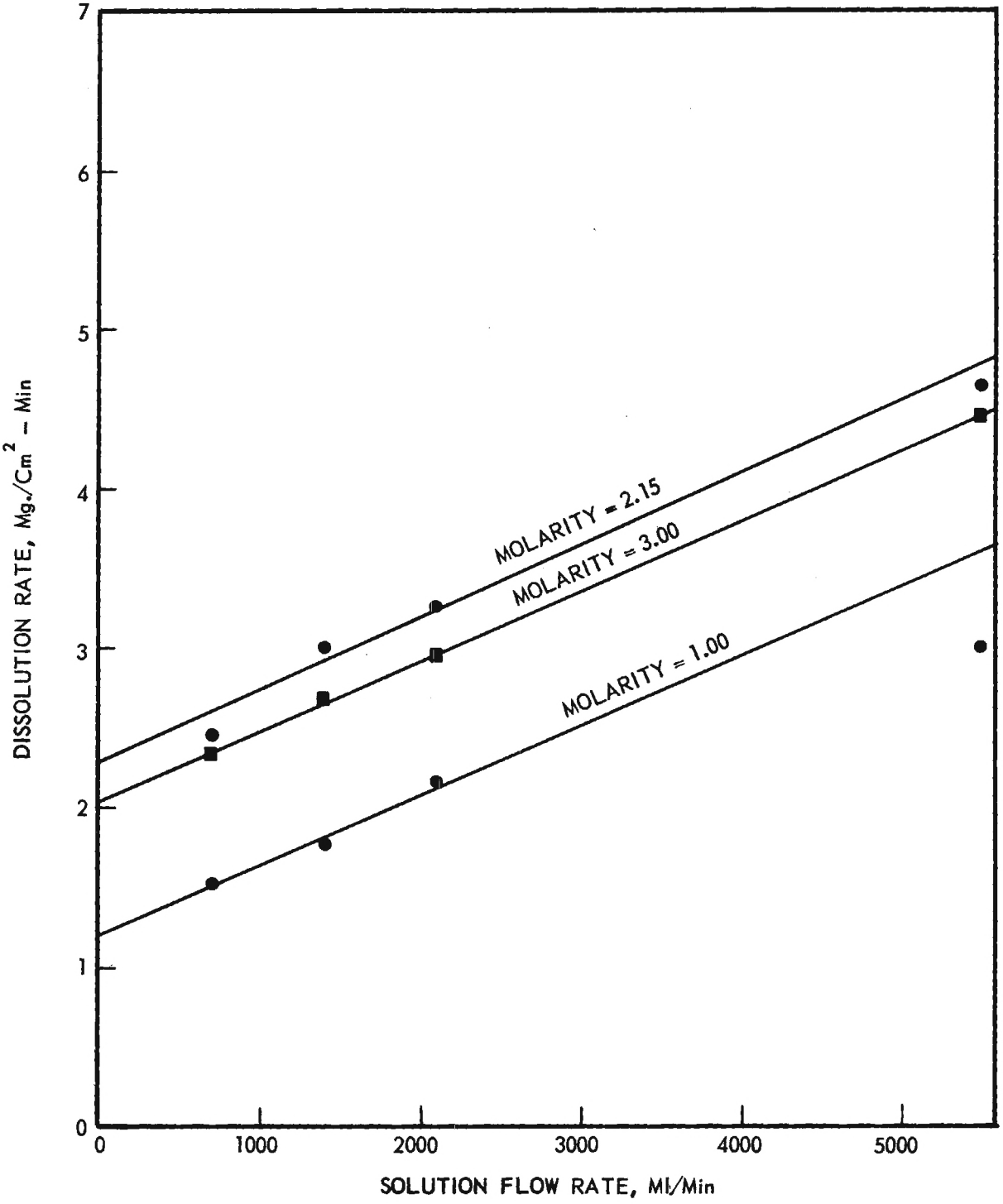

Figure 6. Dissolution Rate Flow Rate Dependency.
Temperature = 25°C.

TABLE III

EFFECT OF SOLUTION FLOW RATE ON THE REACTION RATE

Temperature = 25° C, Nitrogen Blanket

Reaction Time (Min)	$FeCl_3$ Concentration (M)	Flow Rate (Ml/Min)	Dissolution Rate (Mg/Cm^2-Min)
30	0.529	700	.747
30	1.023	700	1.51
30	1.275	700	1.69
30	1.527	700	1.96
30	1.717	700	2.19
30	1.863	700	2.39
30	1.922	700	2.48
30	2.130	700	2.37
30	2.314	700	2.47
30	2.421	700	2.64
30	2.690	700	2.53
30	2.888	700	2.46
30	3.088	700	2.32
30	3.208	700	2.32
30	3.472	700	2.08
30	3.981	700	1.57
30	0.530	1400	1.03
30	1.008	1400	1.77
30	1.229	1400	2.16
30	1.467	1400	2.58
30	1.638	1400	2.67
30	1.654	1400	2.73
30	1.853	1400	2.97
30	1.861	1400	3.06
30	2.035	1400	3.07

(Continued)

TABLE III (Continued)

EFFECT OF SOLUTION FLOW RATE ON THE REACTION RATE

Temperature = 25° C, Nitrogen Blanket

Reaction Time (Min)	$FeCl_3$ Concentration (M)	Flow Rate (Ml/Min)	Dissolution Rate (Mg/Cm^2-Min)
30	2.039	1400	3.14
30	2.106	1400	3.15
30	2.391	1400	3.07
30	2.602	1400	2.67
30	2.800	1400	2.60
30	2.953	1400	2.62
30	3.109	1400	2.48
30	3.310	1400	2.25
30	3.831	1400	1.87
60	.5008	2100	.959
60	.9539	2100	1.94
60	1.254	2100	2.40
60	1.498	2100	2.82
60	1.690	2100	3.17
60	1.888	2100	3.19
60	2.096	2100	3.17
60	2.285	2100	3.24
60	2.501	2100	3.23
60	2.668	2100	2.97
60	2.859	2100	2.95
60	3.050	2100	2.79
60	3.183	2100	2.70
60	3.446	2100	2.27
60	3.986	2100	1.92
30	0.482	5500	1.66
30	1.393	5500	3.95
30	2.031	5500	4.89

(Continued)

TABLE III (Continued)

EFFECT OF SOLUTION FLOW RATE ON THE REACTION RATE

Temperature = 25° C, Nitrogen Blanket

Reaction Time (Min)	$FeCl_3$ Concentration (M)	Flow Rate (Ml/Min)	Dissolution Rate (Mg/Cm^2-Min)
30	2.411	5500	4.50
30	2.976	5500	4.15
30	3.821	5500	3.64

In all the above runs the copper samples were mounted perpendicular to the direction of the solution flow. However, a study of the effect of varying the sample surface position relative to the direction of flow would allow better comparison to Ferrari's work, where all runs were made parallel to the flow direction. Therefore, a series of runs was conducted with the face parallel to the direction of flow. Reaction rate data for these experiments are tabulated in Table IV. Curves showing the difference in dissolution rate for parallel and

TABLE IV

PARALLEL FLOW OF FERRIC CHLORIDE SOLUTIONS

Temperature = 25° C, Nitrogen Blanket
Reaction Time = 30 Minutes

$FeCl_3$ Concentration (M)	Flow Rate (Ml/Min)	Dissolution Rate (Mg/Cm^2-Min)
0.485	1400	0.735
1.433	1400	1.57
1.990	1400	1.91
2.361	1400	1.91
3.074	1400	1.61
3.801	1400	1.26

perpendicular flow are given in Figure 7. The etch rate with the sample perpendicular to the direction of solution flow was from 45 to 63 per cent greater than the values for parallel flow, with an average value of 55 per cent. If one postulates a laminar boundary next to the reaction surface through which the diffusion occurs, it is reasonable to expect a thinner layer for diffusion with the flow normal to the surface than parallel. With a thinner layer, diffusion-controlled reactions would have larger reaction rates. Chemical-controlled reactions would display the same reaction rate with any orientation with respect to the solution flow direction. Therefore, it may again be proposed that the reaction between copper and ferric chloride solutions is diffusion-controlled.

D. Effect of Dissolved Oxygen

Other investigators (10,14) have reported a dependency of the dissolution rate of copper in acids on the dissolved oxygen content. Ferrari (19) concluded from his experiments that the reaction rate of copper in ferric chloride was independent of the dissolved oxygen content. To resolve this conflict it was decided to compare the etch rate of nitrogen-saturated solutions and oxygen-saturated solutions. The final results appear in Table V and are presented in graphical form in Figure 8. The decrease in reaction rates for oxygen-saturated solutions may be explained by postulating oxygen to be a surface poison in the copper-ferric chloride reaction. Upon absorption of the oxygen on the copper surface the oxygen reduces the number of active centers available for the copper-ferric chloride reaction. The reduction in active centers implies a slower reaction and consequently a lower dissolution rate.

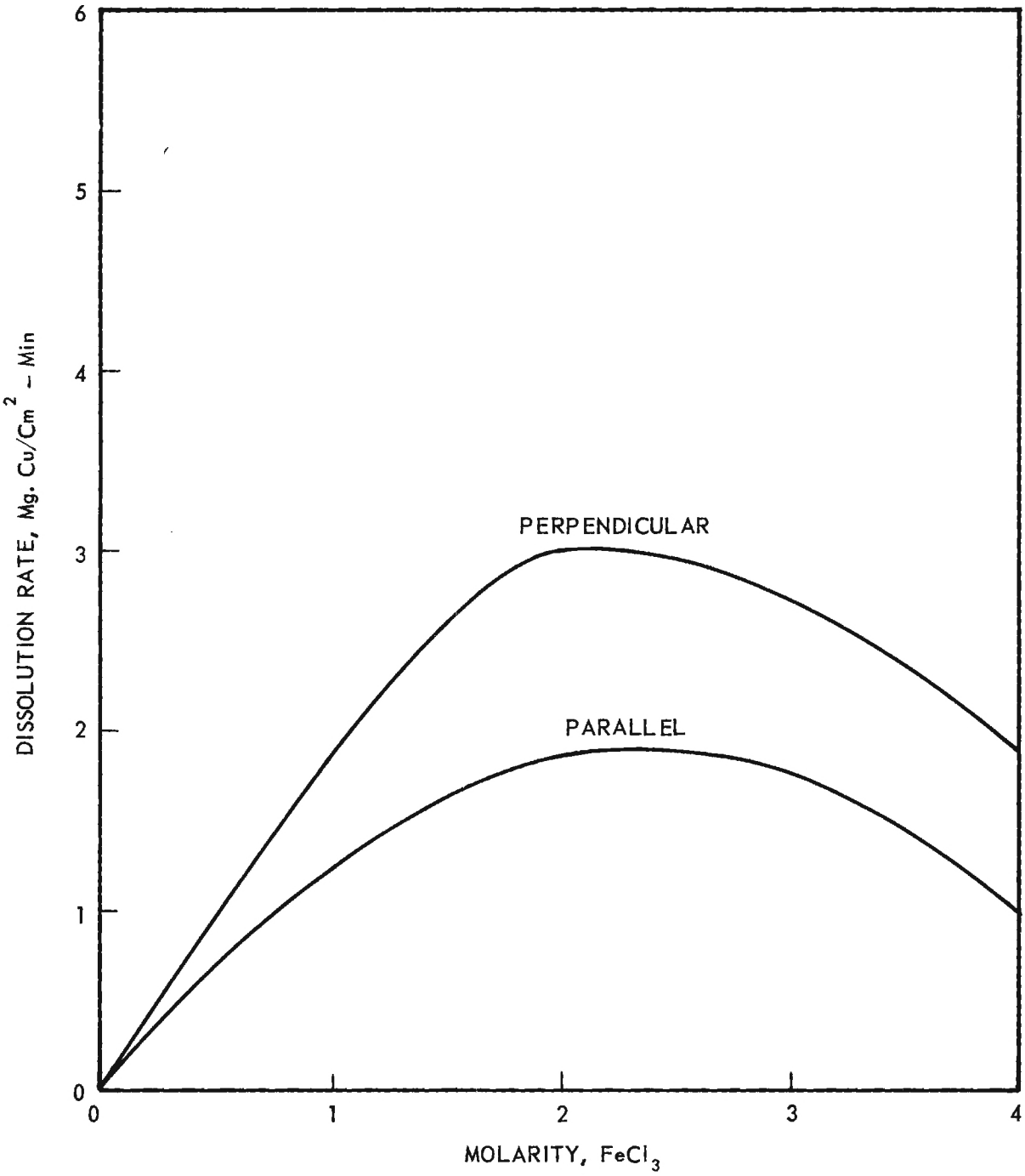

Figure 7. Effect of Sample Position on the Dissolution Rate. Flow = 1400 Ml/Min, Temperature = 25°C, Nitrogen Blanket.

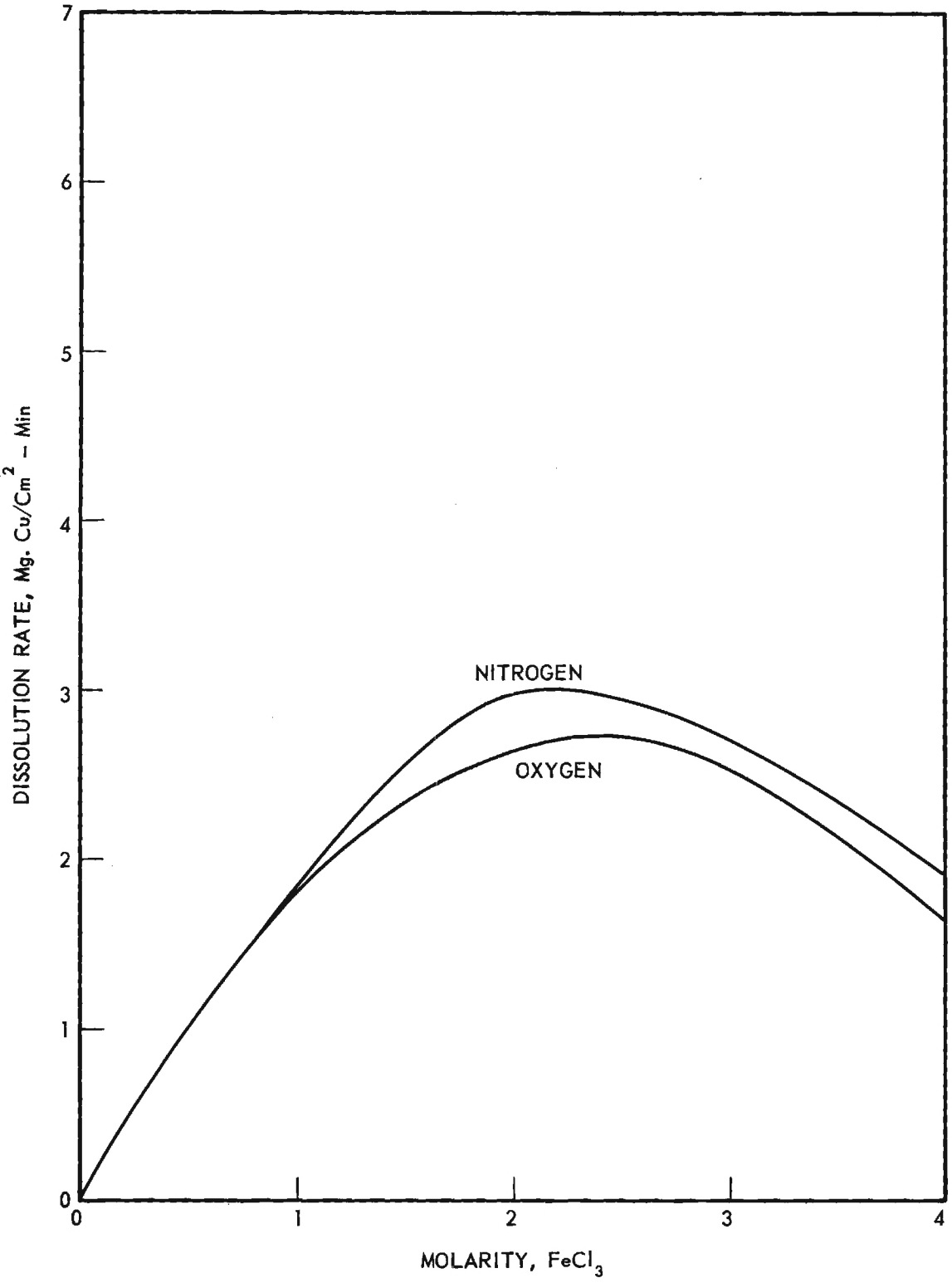

Figure 8. Effect of Oxygen and Nitrogen as Blanket Gases. Flow = 1400 Ml/Min, Temperature = 25°C.

TABLE V

OXYGEN BLANKETED REACTIONS

Temperature = 25° C
Reaction Time = 30 Min

$FeCl_3$ Concentration (M)	Flow Rate (Ml/Min)	Dissolution Rate (Mg/Cm^2-Min)
0.533	1400	1.04
1.484	1400	2.35
2.062	1400	2.76
2.418	1400	2.78
2.986	1400	2.40
3.813	1400	1.78

One would expect dissolved oxygen, reacting in accordance with the equation,

$$2Fe^{++} + \frac{1}{2}O_2 + 2H^+ = 2Fe^{+++} + H_2O$$

to regenerate the ferric ion previously reduced by the copper to ferrous, with the result that the reaction rate would be increased through operation of the mass-action law. There have even been suggestions that commercial etching machines incorporate an aeration feature for this purpose, although this apparently has never been done.

This oxidation, which occurs quite readily in alkaline solution, does not occur to any appreciable extent in acidic media, although the above equation would indicate that high hydrogen ion concentration would favor the forward reaction. Latimer (24) suggests that the reason for this lies in the fact that the oxygen molecule is initially reduced to hydrogen peroxide, which has a potential of

only -0.68 volt, whereas the standard oxidation potential for the reaction $Fe^{++} = Fe^{+++} + e^{-}$ is -0.771 volt, and the equilibrium concentration of hydrogen peroxide is not then sufficient to oxidize ferrous ion. In alkaline medium the very low solubility of ferric hydroxide reduces the potential of the Fe^{++}-Fe^{+++} couple sufficiently to promote rapid oxidation of the ferrous ion.

E. Effects of Solution Density and Viscosity

To calculate the effect of the ferric chloride solution density and viscosity on the mobility of the reacting ions through the diffusion layer, experimental data on the viscosity as a function of the molarity were needed. Basic data were measured on two Ostwald-Cannon-Fenske viscosimeters of different viscosity ranges. Determinations were made at 24° C because of unstable bath temperatures at 25° C. The data from both viscosimeters agreed over the molarity range of 0- to 3.5-molar ferric chloride to within 3 per cent. The density data for ferric chloride solutions versus molarity were determined by the authors at 24° C and are presented with the viscosity data in Table VI. Graphs of the viscosity and density as functions of molarity are given in Figures 9 and 10, respectively.[a]

Schlichting (25) in his text "Boundary Layer Theory" derived an exact solution for stagnation in plane flow normal to a flat plate. His solution showed the stagnant diffusion boundary layer thickness to be a function of the square root of the kinematic viscosity, which is the quotient of the viscosity divided by the density. Also, the thickness was shown to be uniform over the entire surface. Assuming the dissolution rate R(M) is a function of molarity,

[a] Lange's data for viscosity is in disagreement; however, a check of original references shows that Lange's data was apparently derived from Kanitz (Zeitschrift fur Physikalische Chemie, 22, 341 (1897), and was incorrectly interpreted as based upon mole weights rather than gram-equivalent weights. When corrected, it is in close agreement with our experimental data. A similar error was apparently made by the authors of Lange's in the cases of ammonium sulfate and potassium carbonate.

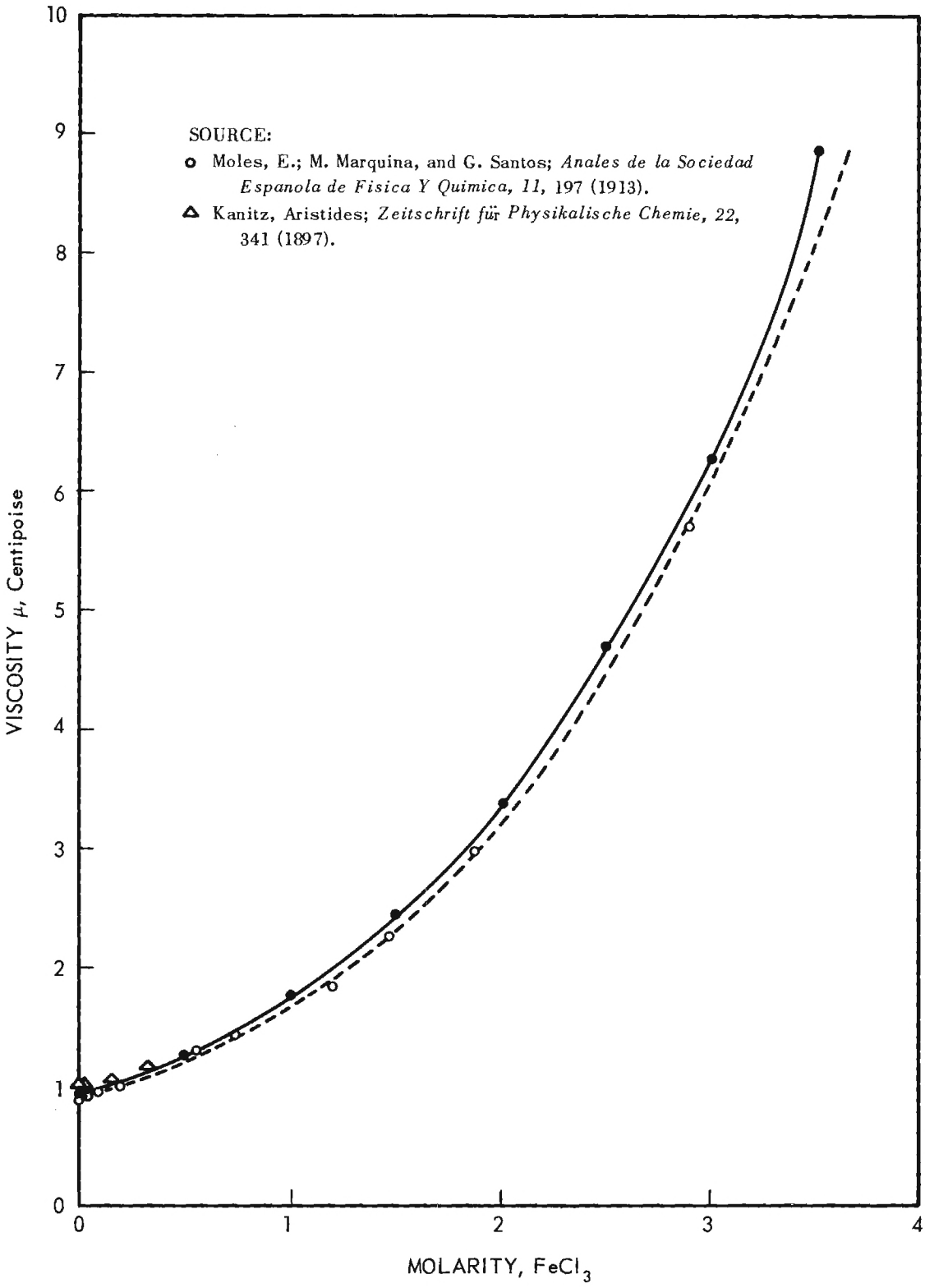

Figure 9. Ferric Chloride Viscosity as Function of Molarity. Temperature = 24°C.

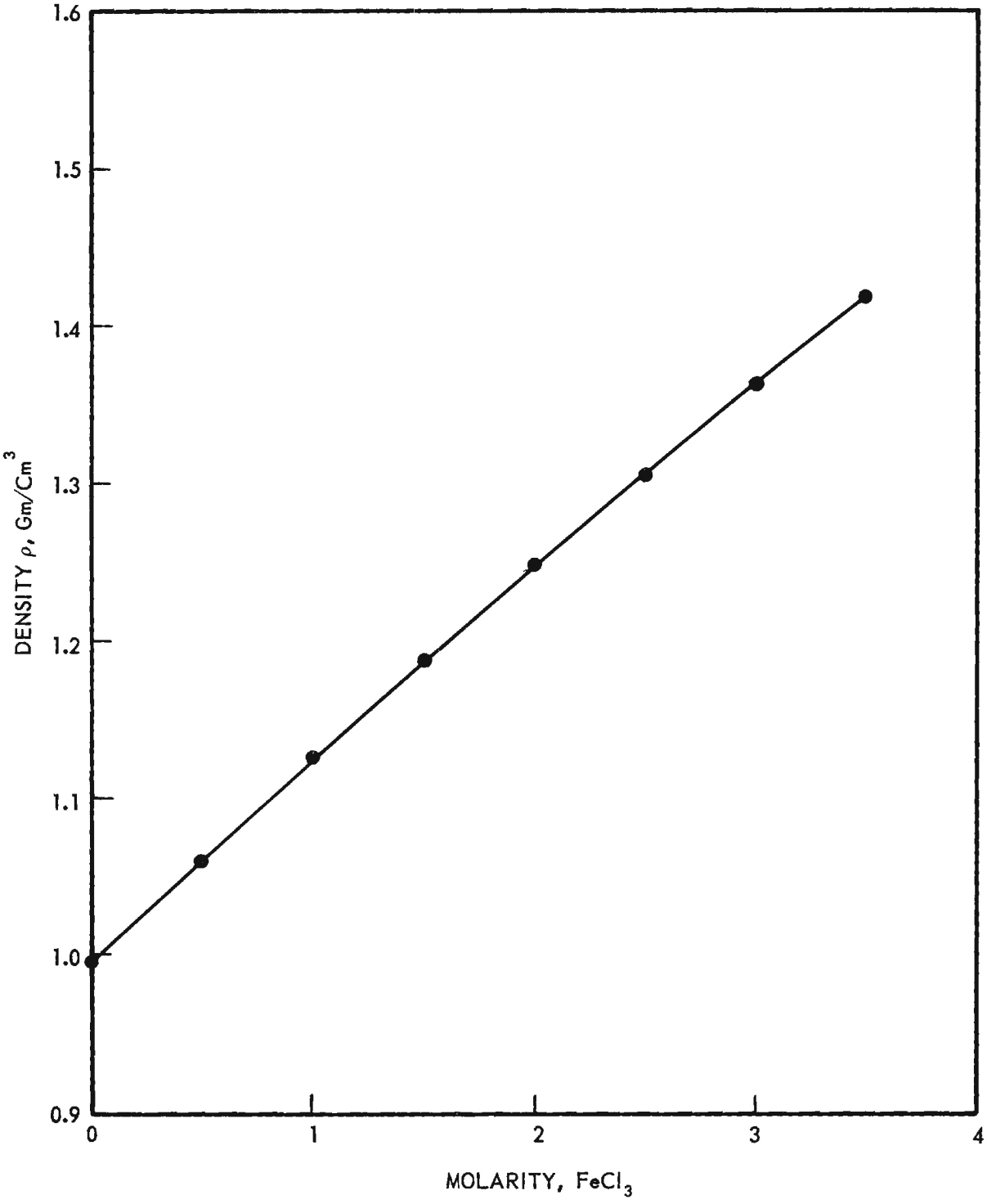

Figure 10. Ferric Chloride Density as Function of Molarity. Temperature = 24°C.

TABLE VI

VISCOSITY AND DENSITY MEASUREMENTS

Temperature = 24° C

$FeCl_3$ Concentration (M)	Viscosity (Centipoise)	Density (Gm/Cm^3)
0	0.9142	0.9973
0.5	1.261	1.060
1.0	1.748	1.127
1.5	2.442	1.187
2.0	3.369	1.248
2.15	3.747	1.266
2.5	4.708	1.306
3.0	6.274	1.363
3.5	8.860	1.419

divided by the diffusion boundary layer thickness δ, or $R(M) = K \frac{F(M)}{\delta}$, the following may be proposed:

$$R(M) = \frac{K\,F(M)}{\delta} = K_1\,F(M)\,(\mu/\rho)^{-\frac{1}{2}},$$

or

$$K_1\,F(M) = (\mu/\rho)^{\frac{1}{2}}\,R(M),$$

noting that the following limit exists:

$$\lim_{M \to 0} F(M) = R(M)$$

Therefore,

$$K_1 = (\mu/\rho)^{\frac{1}{2}}\Big|_{M=0} = 0.9574$$

and

$$F(M) = \frac{R(M)(\mu/\rho)^{\frac{1}{2}}}{0.9574}$$

Based on the above equation the mass transfer corrections (square root of the kinematic viscosity) were calculated and used to calculate the corrected dissolution rate function, F(M), for the runs at 1400 milliliters per minute and 25° C. Values of the correction and the corrected reaction rate at various molarities are given in Table VII. Plots of the mass transfer correction and the corrected dissolution rate function, F(M), are given in Figures 11 and 12 respectively.

TABLE VII

MASS TRANSFER CORRECTION AND CORRECTED DISSOLUTION RATE FUNCTION

Temperature = 25° C, Flow Rate = 1400 Ml/Min

$FeCl_3$ Concentration (M)	$(\mu/\rho)^{\frac{1}{2}}$	Dissolution Rate (Mg/Cm^2-Min)	
		R(M)	F(M)
0	0.9574	0	0
0.5	1.091	1.01	1.15
1.0	1.245	1.82	2.37
1.5	1.434	2.57	3.85
2.0	1.643	2.99	5.13
2.15	1.720	3.00	5.39
2.5	1.899	2.95	5.85
3.0	2.146	2.70	6.05
3.5	2.498	2.34	6.11

F. Reacting Species in Solution

The dissolution rate, F(M), shown in Figure 12, increases almost linearly with increasing molarity up to a molarity of about two. Above two molar the rate increases more slowly, apparently approaching an asymptote at high ferric

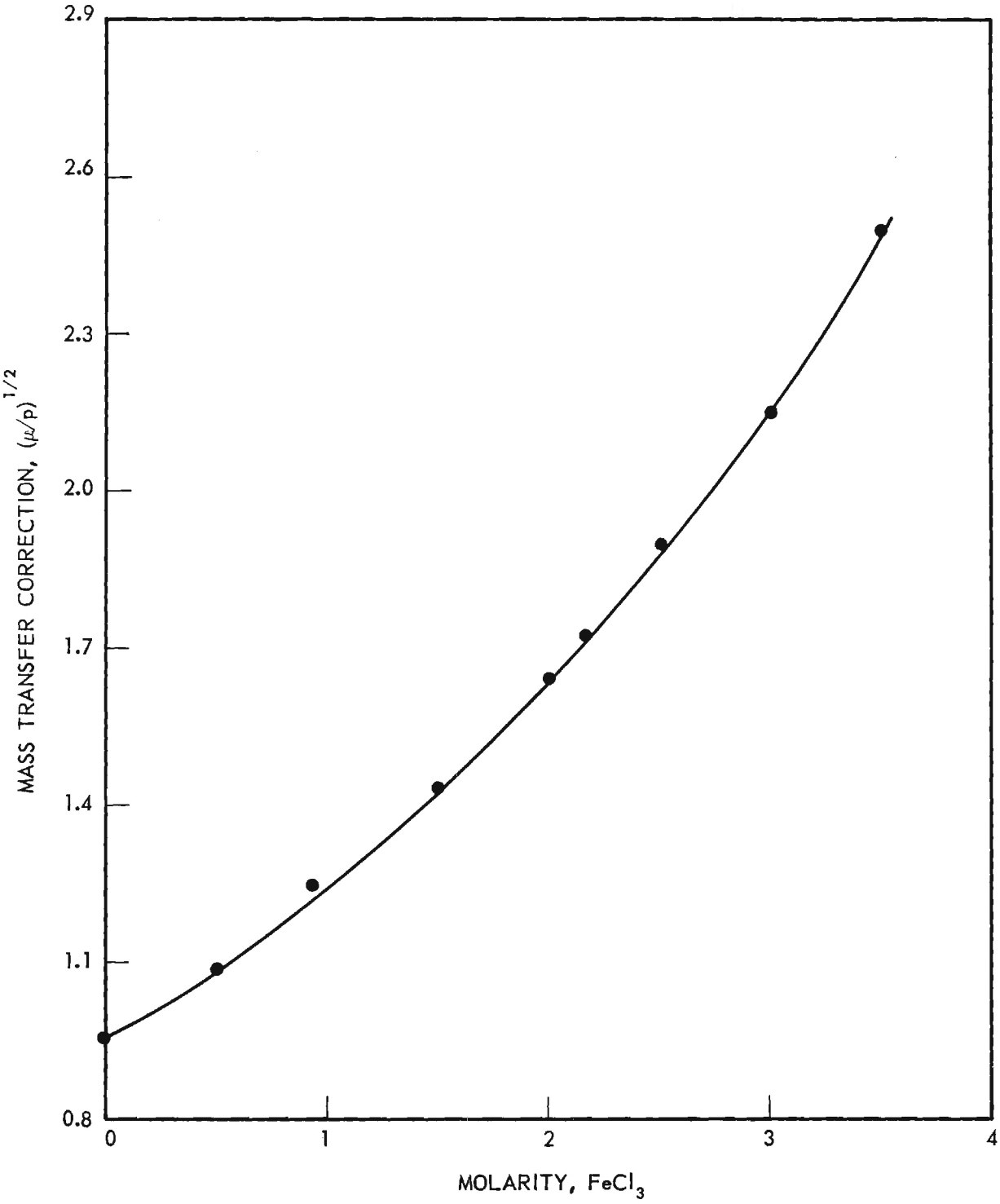

Figure 11. Mass Transfer Correction as Function of Molarity.

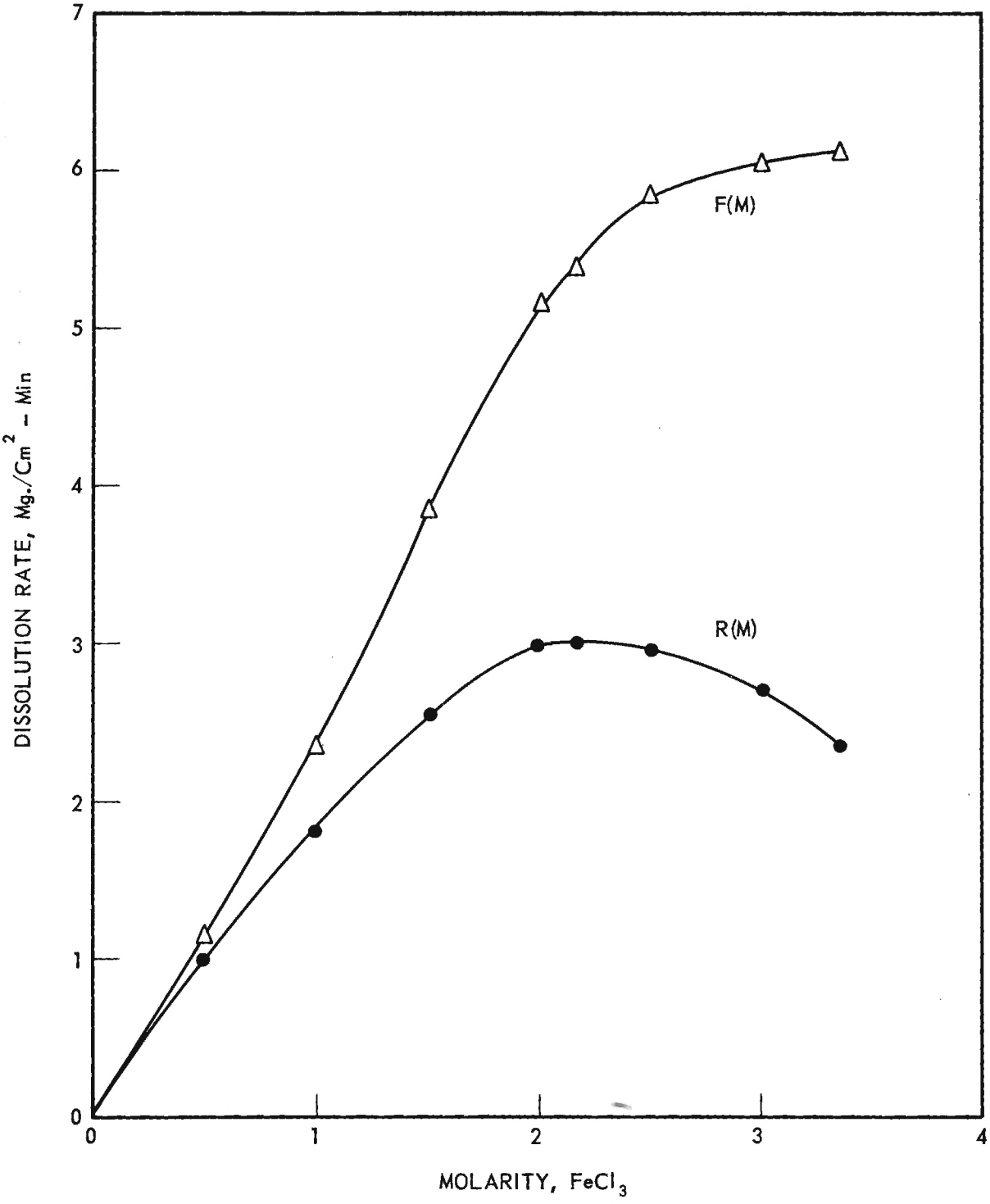

Figure 12. Dissolution Rate Function, F(M).

chloride concentrations. An explanation of the corrected dissolution rate curve may be proposed based on Brooks' conclusion (18) of the reactive species. He proposed the active species to be Fe^{+3}, $FeCl^{+2}$, and $FeCl_2^{+}$. The species $FeCl_3$ was postulated as having a negative reactivity or inhibiting effect upon the reaction. It is proposed that this is equivalent to the increasing density and viscosity effect on the diffusion layer thickness with increasing molarity. Brooks discussed the increased diffusion barrier with respect to an increasing amount of ferric chloride molecules. The other species present also increase the density and viscosity and, with ferric chloride directly determine the diffusion layer thickness. It is postulated that ferric chloride molecules do not react with the copper surface and their only effect is one of contribution to the density and viscosity of the solution.

In aqueous solutions ferric chloride dissociates to a varying degree dependent upon the molarity of the solution. An equilibrium reaction may be visualized as the following simplified equation between ferric chloride and its chloro complexes:

$$FeCl_3 = Fe^{+3} + FeCl^{+2} + FeCl_2^{+} + FeOH^{+2}$$

As the molarity increases the species present change from only Fe^{+3} and $FeOH^{+2}$ at zero molarity to varying amounts of all the above five. At first the largest fraction of the species is of the ions Fe^{+3} and $FeOH^{+2}$ with $FeCl^{+2}$ having the largest portion at higher molarities, followed by $FeCl_2^{+}$ and finally ferric chloride at very high concentrations. From Figure 12 it is seen that a slight increase in the slope occurs between 0.5 and 1.5 molar ferric chloride. At these concentrations the ferric chloro species, $FeCl^{+2}$, is more abundant

than the Fe^{+3} and $FeOH^{+2}$ that occur at very low concentrations. Therefore it may be concluded that $FeCl^{+2}$ is more reactive than the combined effect of Fe^{+3} and $FeOH^{+2}$. As the ferric chloride molarity increases further, the dominant species becomes $FeCl_2^{+}$, which appears to be slightly less reactive than $FeCl^{+2}$. Above a molarity of 2.0 the rate of increase of the dissolution rate, F(M), decreases. This is attributed to the mass action effect at high concentrations where an increase in the ferric chloride concentration brings only a very slight increase in the ferric chloro complexes.

The asymptote previously noted occurs, therefore, because of the very small change in active species at higher concentrations.

IV. STUDIES OF INHIBITORS

A. Effect of Formamidine Disulfide

A preliminary study of the inhibitors was conducted at 25° C and a flow rate of 1400 milliliters per minute. This investigation indicated that formamidine disulfide, the reaction product of thiourea and ferric chloride, would be the principal inhibitor studied. The elementary experiments revealed a basic difference between the action of thiourea and formamidine disulfide. Thiourea retarded the copper dissolution rate over its entire range of concentration, showing a sharply decreasing rate with increasing concentration until a minimum is obtained around 0.7 gram of thiourea per liter of solution. Beyond this point additional thiourea did not change the reaction rate. It is postulated that at this concentration enough inhibitor is present to coat the entire metallic copper surface and prevent a rapid dissolution of copper. At this point there is a much thicker coating than that of the cuprous chloride (19) normally present on the metallic copper surface, and it is reasonable to expect a large rate reduction with increase in the amount of film present.

Formamidine disulfide, however, enhanced the reaction at concentrations up to approximately the same critical concentration as for thiourea. A very sharp discontinuity occurred at this point, and any additional inhibitor reduced the reaction rate to the minimum observed with thiourea.

The inhibiting effect of formamidine disulfide had not been previously investigated with apparatus similar to that used in these experiments. For this purpose a statistical design consisting of 20 experiments was prepared in the hope of obtaining a prediction equation (a fitted polynomial) relating the variables, reaction time, ferric chloride molarity, and formamidine disulfide concentration. The levels of the three variables were in the proportions of -1.633, -1.0, 0, +1.0, +1.633. The experiment in which each of the three variables was in the amount of the center, or zero, value had six replications for the purpose of measuring experimental error.

Both the copper dissolution rate and the radioactivity of the film present on the metallic surface were measured in each experiment. The radioactivity had a wide range in the six replicated experiments used to measure the experimental error and no obvious correlation with changes in variables. Upon removal of the sample from the reaction cell the film was noticed to be partially removed during washing and not to be as adherent as the cuprous oxide normally present in the uninhibited reaction of copper with ferric chloride. Subsequently no further work was attempted using radioactive-tracer-labeled inhibitors. Sufficient data were obtained by following only the dissolution rate.

A prediction curve was fitted to the data of the above 20 experiments, using the reaction rate as the dependent variable. However, the lack of fit of this equation was significant and the prediction equation was discarded.

The sharp discontinuity observed and previously mentioned did not allow a smooth curve of any type to be fitted as a prediction equation. The purpose in trying to obtain a prediction equation had been to produce curves showing the effects of each variable on the reaction rate with as few experiments as possible. Failure with the attempted equation made it necessary to use a series of experiments in which one variable at a time was changed.

The results of the first 20 experiments at 25° C and 1400 milliliters per minute are tabulated in Table VIII. From observation of these first experiments it is noted that the dissolution rate decreases with increasing time.

In comparing experiments in which the molarity was changed it is generally noted that the maximum reaction rate occurred between 2.0- and 2.3-molar ferric chloride. The results seem to indicate that graphs of the etch rate versus ferric chloride molarity with inhibitor would have the same general shape as those previously reported with no inhibitor added. The curves with no inhibitor have a miximum around 2.15-molar ferric chloride. Because of this and a desire to use as many results already obtained as possible, a molarity of 2.15 was used in all successive experiments.

Experiments were conducted with all variables held constant except the flow rate. Data for runs at 25° C and a flow rate of 1400 milliliters per minute are presented in Table IX. Data at a flow rate of 2100 milliliters per minute are tabulated in Table X. Graphs of the data in Tables IX and X are given in Figures 13 and 14 respectively.

In these figures the curves are drawn arbitrarily. For both graphs, however, it is felt that the reaction slowly decreases with increase in formamidine disulfide concentration until a minimum occurs around 0.17 gram per liter. The dissolution rate then increases to a maximum around 0.41 gram formamidine

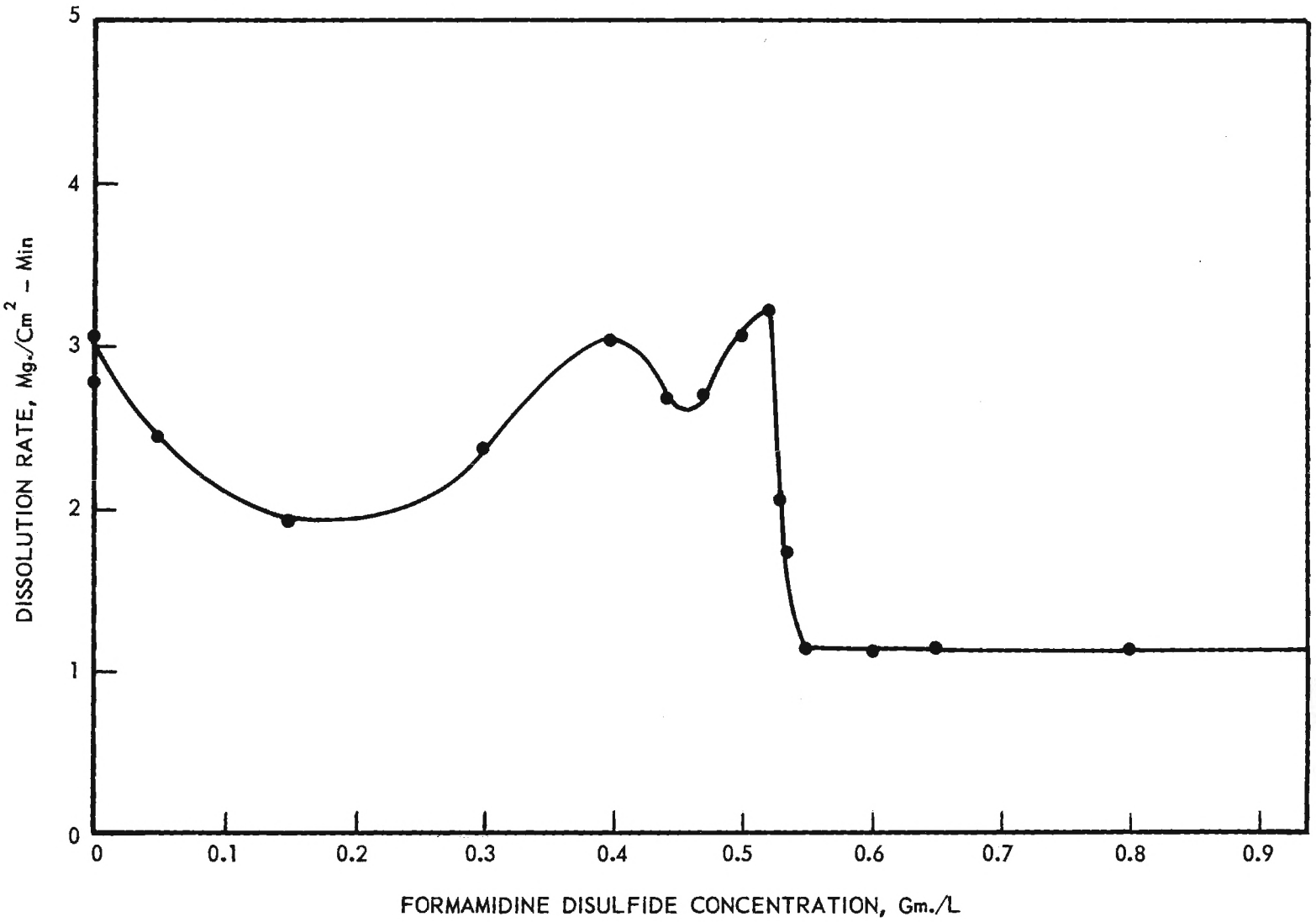

Figure 13. Formamidine Disulfide Effect at 1400 Ml/Min and 25°C. Flow = 1400 Ml/Min, Temperature = 25°C, Reaction Time = 12.75, Molarity = 2.15.

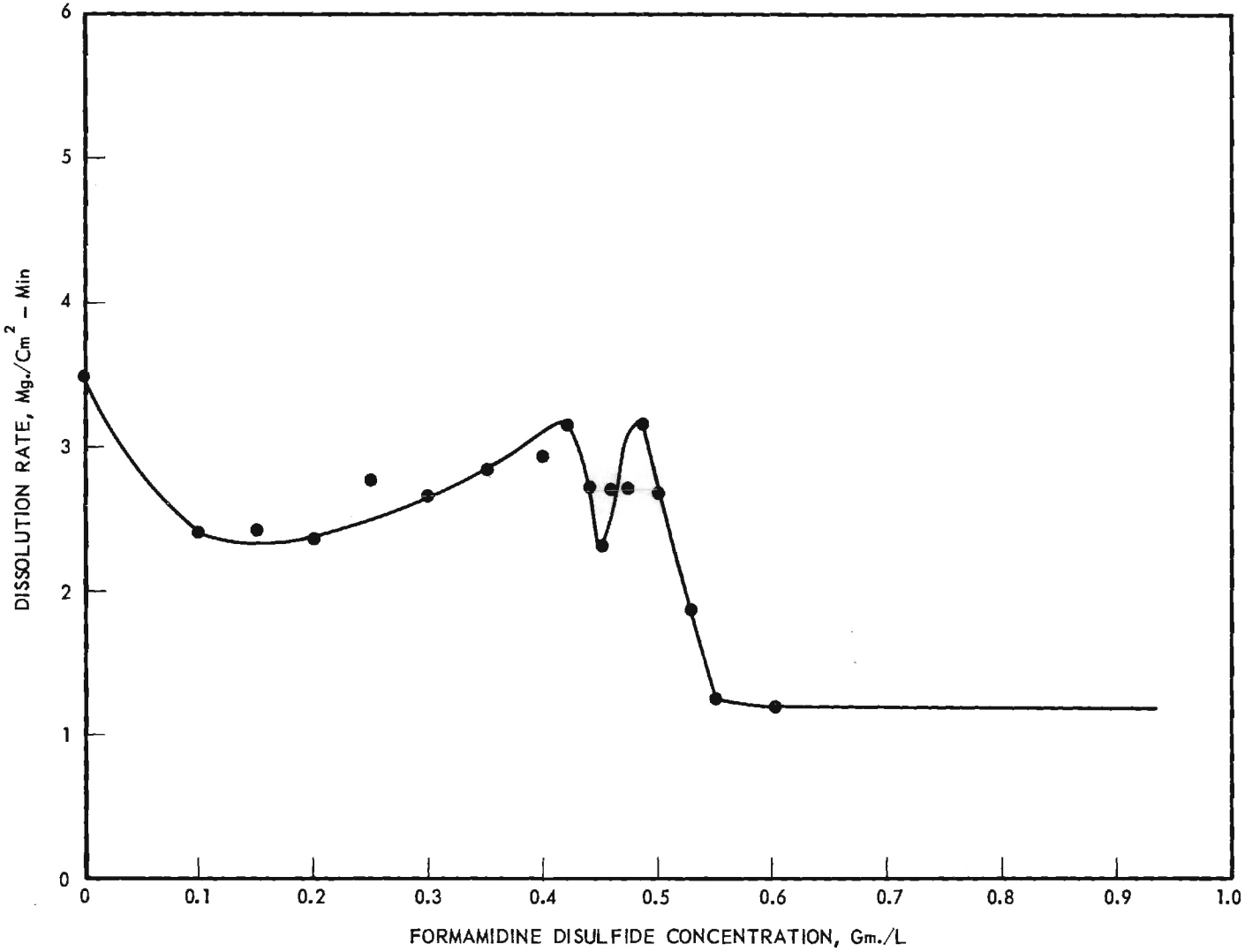

Figure 14. Formamidine Disulfide Effect at 2100 Ml/Min and 25°C. Flow = 2100 Ml/Min, Temperature = 25°C, Reaction Time = 12.75, Molarity = 2.15.

TABLE VIII

FORMAMIDINE DISULFIDE INHIBITOR STUDY, PART A

Temperature = 25°C, Flow Rate = 1400 Ml/Min

$FeCl_3$ Concentration (M)	Reaction Time (Min)	Inhibitor Concentration (Gm/L)	Dissolution Rate (Mg/Cm^2-Min)
1.90	12.75	0.400	2.42
2.00	5.25	0.155	2.43
2.00	5.25	0.155	2.39
2.00	5.25	0.645	1.34
2.00	20.25	0.155	1.85
2.00	20.25	0.645	1.00
2.00	20.25	0.645	1.04
2.00	20.25	0.645	1.22
2.15	0.50	0.400	4.93
2.15	12.75	0.000	3.04
2.15	12.75	0.400	2.98
2.15	12.75	0.400	3.07
2.15	12.75	0.400	2.99
2.15	12.75	0.400	2.39
2.15	12.75	0.400	3.46
2.15	12.75	0.400	2.93
2.15	12.75	0.800	1.17
2.15	25.00	0.400	1.81
2.30	5.25	0.155	2.52
2.30	5.25	0.645	1.73
2.30	5.25	0.645	3.07
2.30	5.25	0.645	1.46
2.30	20.25	0.155	2.06
2.30	20.25	0.155	2.00
2.30	20.25	0.645	1.65
2.40	12.75	0.400	3.00

TABLE IX

FORMAMIDINE DISULFIDE INHIBITOR STUDY, PART B

Temperature = 25° C, Flow Rate = 1400 Ml/Min
$FeCl_3$ Concentration = 2.15 Moles/L

Reaction Time (Min)	Inhibitor Concentration (Gm/L)	Dissolution Rate (Mg/Cm^2-Min)
12.75	0.000	3.04
12.75	0.050	2.47
12.75	0.150	1.96
12.75	0.300	2.37
12.75	0.400	3.07
12.75	0.440	2.71
12.75	0.470	2.71
12.75	0.500	3.05
12.75	0.520	3.22
12.75	0.530	2.05
12.75	0.540	1.72
12.75	0.550	1.18
12.75	0.600	1.12
12.75	0.645	1.15
12.75	0.800	1.17

disulfide per liter and suddenly decreases for slightly higher concentrations. A rapid rise then follows to a maximum around 0.50 gram per liter, after which the rate decreases sharply to a constant value for all higher concentrations of inhibitor.

The 50 per cent change in ferric chloride flow rate makes no appreciable change in the positions of maxima and minima of the reaction rate. However, distinctive changes in the shape of the curve are noticeable. At the

TABLE X

FORMAMIDINE DISULFIDE INHIBITOR STUDY,
FLOW RATE EFFECT

Temperature = 25°C, Flow Rate = 2100 Ml/Min
$FeCl_3$ Concentration = 2.15 Moles/L

Reaction Time (Min)	Inhibitor Concentration (Gm/L)	Dissolution Rate (Mg/Cm^2-Min)
12.75	0.00	3.50
12.75	0.10	2.41
12.75	0.15	2.42
12.75	0.20	2.35
12.75	0.25	2.78
12.75	0.30	2.66
12.75	0.35	2.83
12.75	0.40	2.94
12.75	0.42	3.18
12.75	0.44	2.73
12.75	0.45	2.30
12.75	0.45	1.21
12.75	0.45	1.23
12.75	0.46	3.13
12.75	0.46	2.73
12.75	0.48	1.85
12.75	0.48	2.71
12.75	0.49	3.16
12.75	0.50	2.68
12.75	0.53	1.84
12.75	0.55	1.26
12.75	0.60	1.22
12.75	1.00	1.18

lower flow rate, represented in Figure 13, the reaction rate with no inhibitor is slightly less than the peak occurring around 0.50 gram per liter formamidine disulfide. The drop in dissolution rate past this peak is very abrupt. The zero concentration rate of Figure 14 (2100 milliliters per minute) is greater than either of the two maxima at higher concentrations, and the rapid change in etch rate past the second peak is not as abrupt as in the case of the lower flow rate. Although arbitrarily drawn, the sharp dip, previously noted at approximately 0.41 gram per liter inhibitor, does occur. The only question of these data concerns the minimum value that occurs. The reaction may be slower than depicted, but the present apparatus used could not define this area exactly.

In order that the reaction time effect might be studied, experiments were conducted at 0.0, 0.20 and 0.40 gram per liter of formamidine disulfide, holding the temperature and flow rate constant at 25° C and 1400 milliliters per minute respectively. These data are presented in Table XI for a constant ferric chloride molarity of 2.15.

B. Instantaneous Reaction Rate

The determination of any reaction rate necessarily is a measurement of the average rate between the present and the nearest preceding determination. As the frequency of sampling increases (the sampling period decreases) the average reaction rate approaches the instantaneous rate. For an infinite number of samples the average rate over any sampling period is the instantaneous reaction rate. Mathematical treatment of data collected over finite periods will yield instantaneous values of the dissolution rate. This instantaneous rate allows better insight into the actual reaction occurring at a given time regardless of previous history.

TABLE XI

FORMAMIDINE DISULFIDE INHIBITOR STUDY
REACTION TIME EFFECT

Temperature = 25°C, Flow Rate = 1400 Ml/Min
$FeCl_3$ Concentration = 2.15 Moles/L

Reaction Time (Min)	Inhibitor Concentration (Gm/L)	Dissolution Rate (Mg/Cm^2-Min)
0.50	0.000	3.99
0.50	0.000	4.08
2.00	0.000	3.11
4.00	0.000	2.62
8.00	0.000	2.69
8.00	0.000	2.74
12.00	0.000	2.77
12.00	0.000	2.83
12.75	0.000	2.80
12.75	0.000	3.04
20.00	0.000	2.79
30.00	0.000	2.76
45.00	0.000	2.64
0.50	0.200	4.79
4.00	0.200	2.72
12.00	0.200	2.15
20.00	0.200	2.02
30.00	0.200	1.71
0.50	0.400	4.04
0.50	0.400	4.93
0.50	0.400	5.38
1.00	0.400	3.32
4.00	0.400	3.61
5.00	0.400	2.80
8.00	0.400	3.30

(Continued)

TABLE XI (Continued)

FORMAMIDINE DISULFIDE INHIBITOR STUDY,
REACTION TIME EFFECT

Temperature = 25° C, Flow Rate = 1400 Ml/Min
$FeCl_3$ Concentration = 2.15 Moles/L.

Reaction Time (Min)	Inhibitor Concentration (Gm/L)	Dissolution Rate (Mg/Cm^2-Min)
12.75	0.400	2.98
12.75	0.400	3.07
12.75	0.400	2.99
12.75	0.400	2.39
12.75	0.400	3.46
12.75	0.400	2.93
15.00	0.400	3.13
17.00	0.400	2.90
17.00	0.400	2.32
19.00	0.400	2.45
21.00	0.400	2.35
23.00	0.400	2.27
25.00	0.400	1.81
25.00	0.400	2.40
26.00	0.400	2.14
30.00	0.400	1.83
30.00	0.400	2.81
35.00	0.400	1.46
60.00	0.400	1.27

Let $\overline{R}_n$ be the average of n time-interval rate measurements, and $\overline{R}_{n-1}$ be the average of n - 1 measurements. Then

$$\overline{R}_n = \frac{R_1 + R_2 + \ldots + R_n}{n}$$

and

$$\bar{R}_{n-1} = \frac{R_1 + R_2 + \ldots + R_{n-1}}{n - 1} .$$

Then

$$\bar{R}_n - \bar{R}_{n-1} = \frac{R_1 + R_2 + \ldots + R_n}{n} - \frac{R_1 + R_2 + \ldots + R_{n-1}}{n - 1}$$

$$= \frac{(n - 1)R_n + (n-1)(R_1 + R_2 + \ldots + R_{n-1}) - n(R + R + \ldots + R_{n-1})}{n(n - 1)}$$

$$= \frac{(n - 1)R_n - (R_1 + R_2 + \ldots + R_{n-1})}{n(n-1)}$$

$$= \frac{R_n - \bar{R}_{n-1}}{n} ,$$

or

$$n\bar{R}_n - n\bar{R}_{n-1} = R_n - \bar{R}_{n-1},$$

whence

$$R_n = n(\bar{R}_n - \bar{R}_{n-1}) + \bar{R}_{n-1} .$$

If the increment in average rate resulting from addition of the nth rate measurement is defined as $\Delta\bar{R} = (\bar{R}_n - \bar{R}_{n-1})$, then

$$R_n = \bar{R}_{n-1} + n\Delta\bar{R} .$$

If R_n is measured at time t, and $\bar{R}_{n-1}$ is the average rate through time $(t - \Delta t)$, then $\Delta\bar{R} = \Delta t \frac{d\bar{R}}{dt}$. Thus

$$R_t \equiv R_n = \bar{R}_t - \Delta t + n\Delta t \frac{d\bar{R}}{dt} .$$

Now, the curve for $\bar{R}$ actually represents an average of an infinite number of rate measurements taken at infinitesimal time intervals, as the method of measuring $\bar{R}$ (by weight of copper dissolved) is a self-integrating determination. Hence, as Δt approaches 0 and n simultaneously approaches infinity, $n\Delta t$ approaches the value of t. Therefore, in the limit,

$$R_t = \bar{R}_t + t \frac{d\bar{R}}{dt}.$$

In other words, the instantaneous rate at time t is the average rate at that time plus the product of the slope of the average rate and the reaction time. This expression provides a means of computing the instantaneous rate from a plot of average rates versus time.

To determine the instantaneous rate, the slope of the average rate at various times must be found by use of a plot of the average reaction rate versus time. Graphs of the average dissolution rate and the instantaneous rate for no inhibitor are given in Figures 15 and 16. For 0.20 gram per liter formamidine disulfide the average and instantaneous rates are given by Figures 17 and 18; and for 0.40 gram per liter formamidine disulfide Figures 19 and 20 give the average and instantaneous reaction rates respectively.

Figure 15 shows that the reaction rate greatly decreases over the first 3 minutes, reaches a minimum, and then increases slowly. A maximum at 12 minutes is followed by gradually decreasing dissolution rate. Application of the previously derived method for determination of the instantaneous rate gives Figure 16. This graph shows that the instantaneous rate curve has the general shape of the average rate curve, but the maximum and minimum are more pronounced and occur sooner than for the average rate. Explanation of the instantaneous rate curve is based on the build-up in the cuprous chloride film present on the

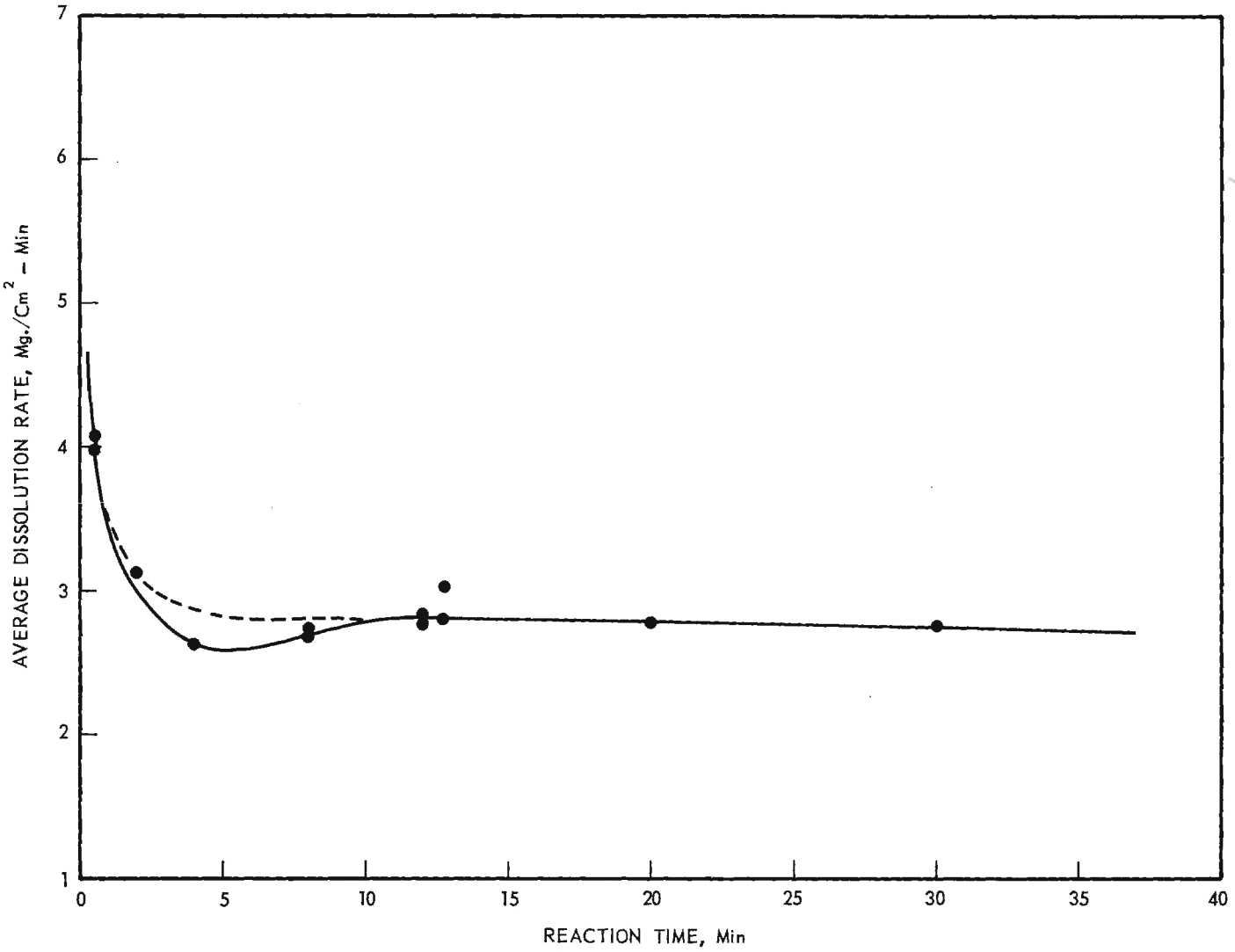

Figure 15. Reaction Time Effect, No Inhibitor Present.
Flow = 1400 Ml/Min, Temperature = 25°C, Molarity = 2.15.

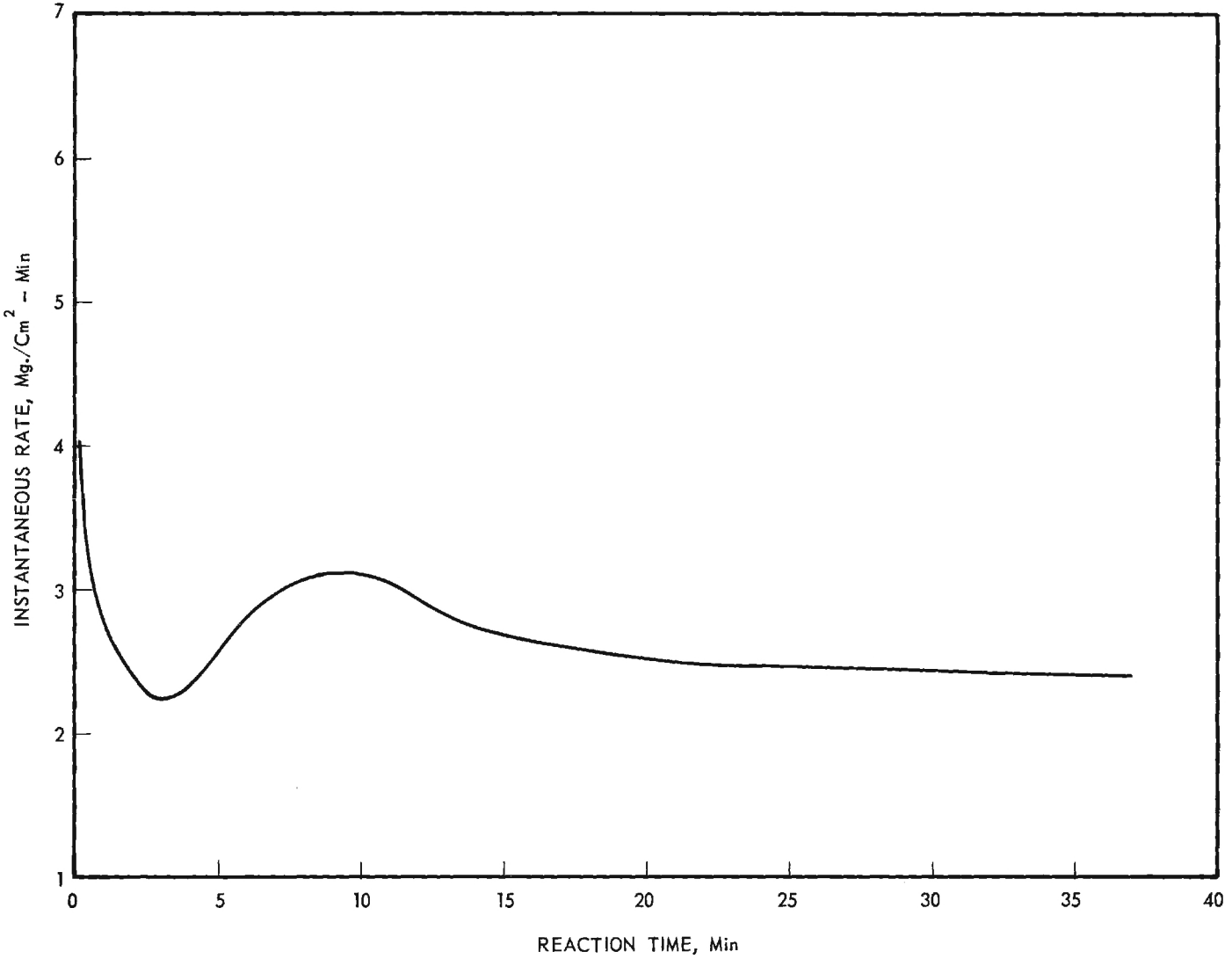

Figure 16. Instantaneous Effect, No Inhibitor Present.
Flow = 1400 Ml/Min, Temperature = 25°C, Molarity = 2.15.

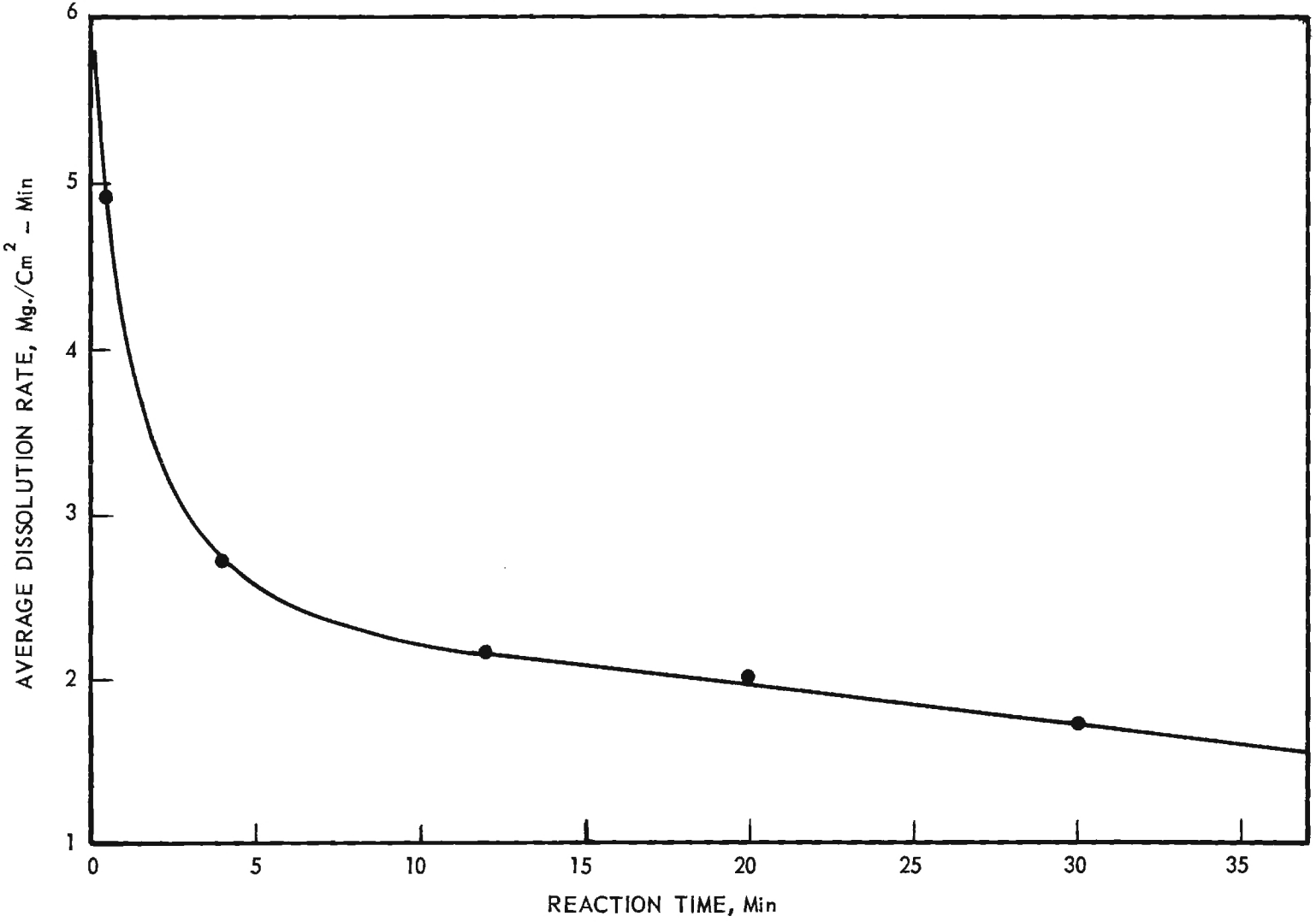

Figure 17. Reaction Time Effect, 0.2 Gm/L Formamidine Disulfide. Flow = 1400 Ml/Min, Temperature = 25°C, Molarity = 2.15.

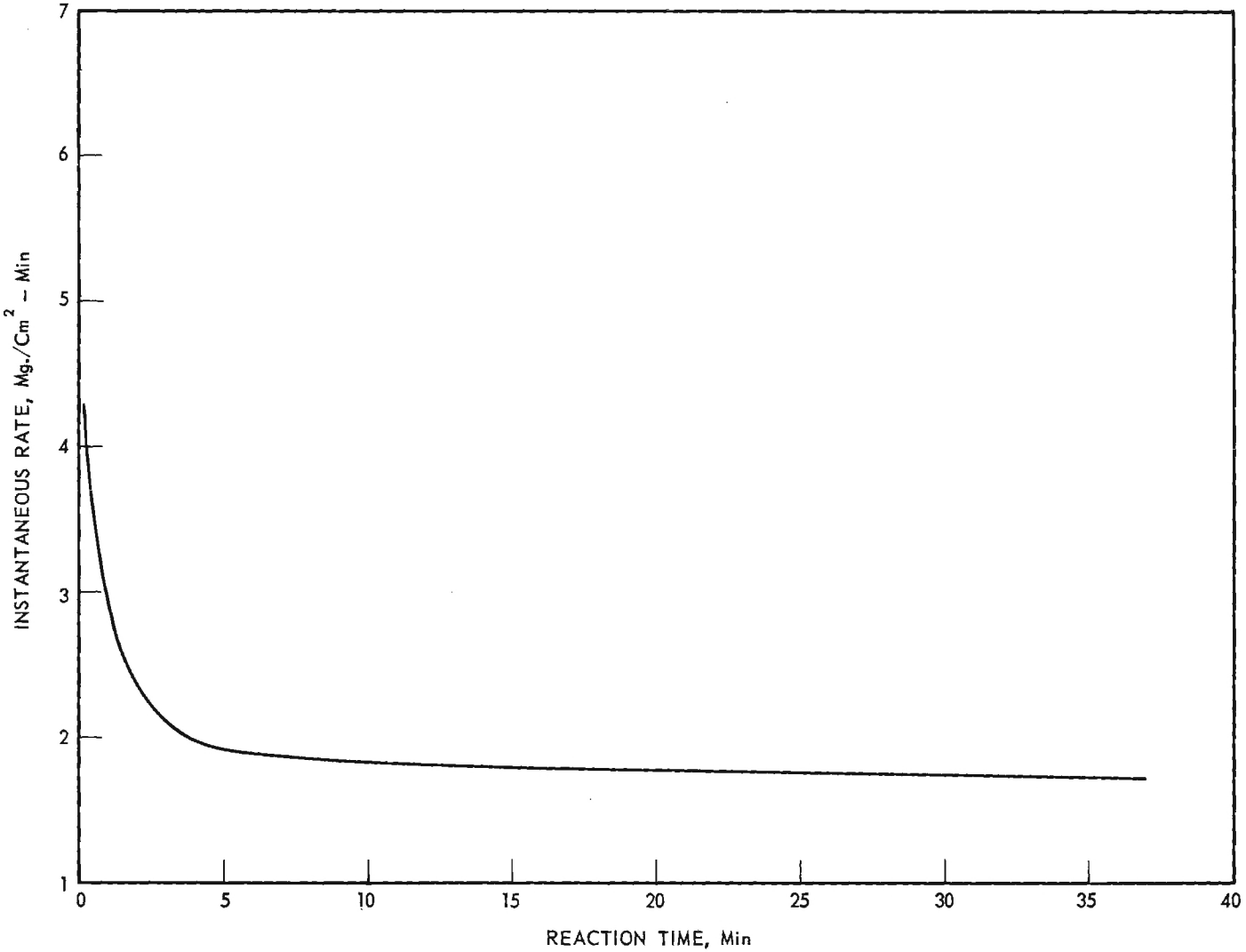

Figure 18. Instantaneous Effect, 0.2 Gm/L Formamidine Disulfide. Flow = 1400 ml/Min, Temperature = 25°C, Molarity = 2.15.

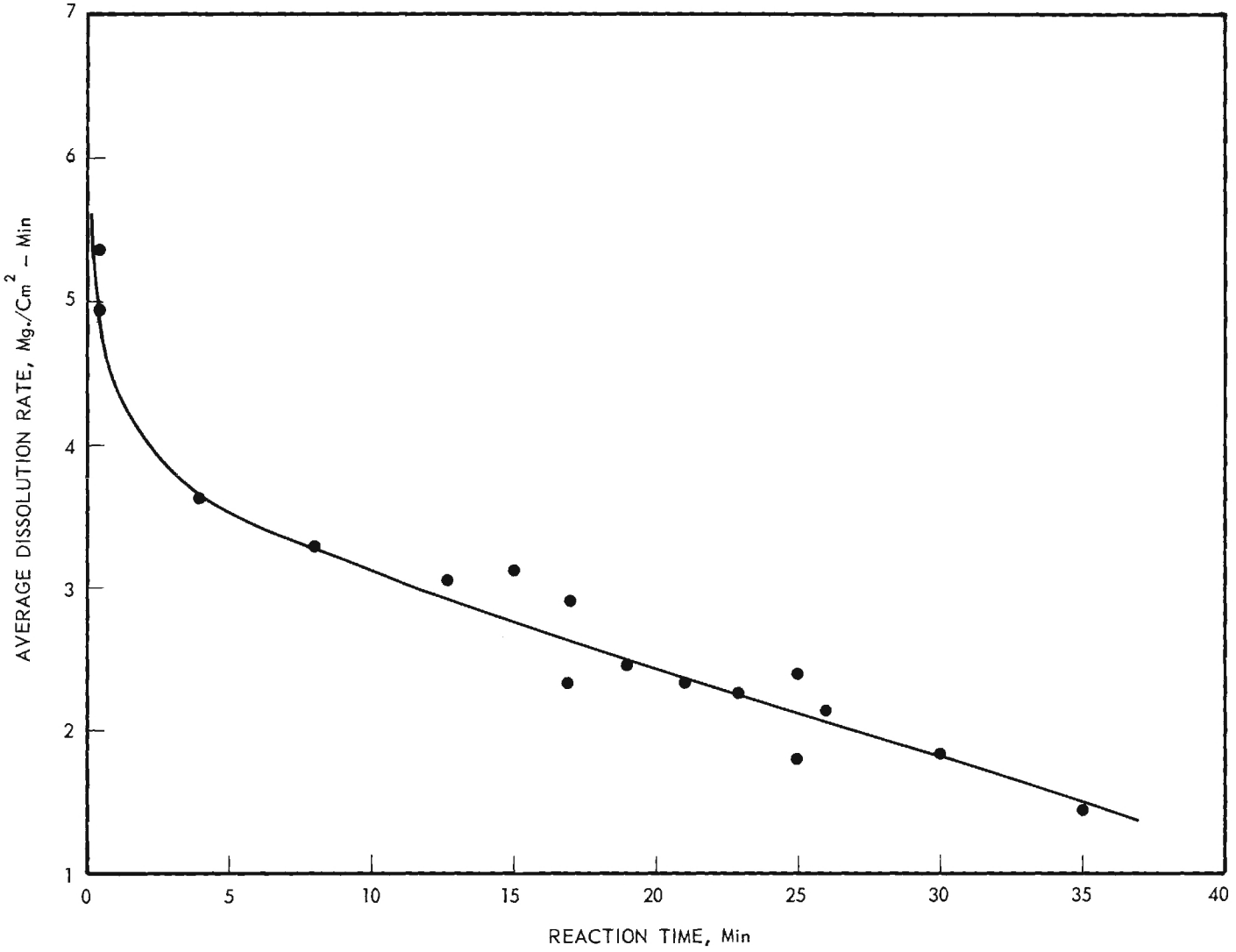

Figure 19. Reaction Time Effect, 0.4 Gm/L Formamidine Disulfide. Flow = 1400 Ml/Min, Temperature = 25°C, Molarity = 2.15.

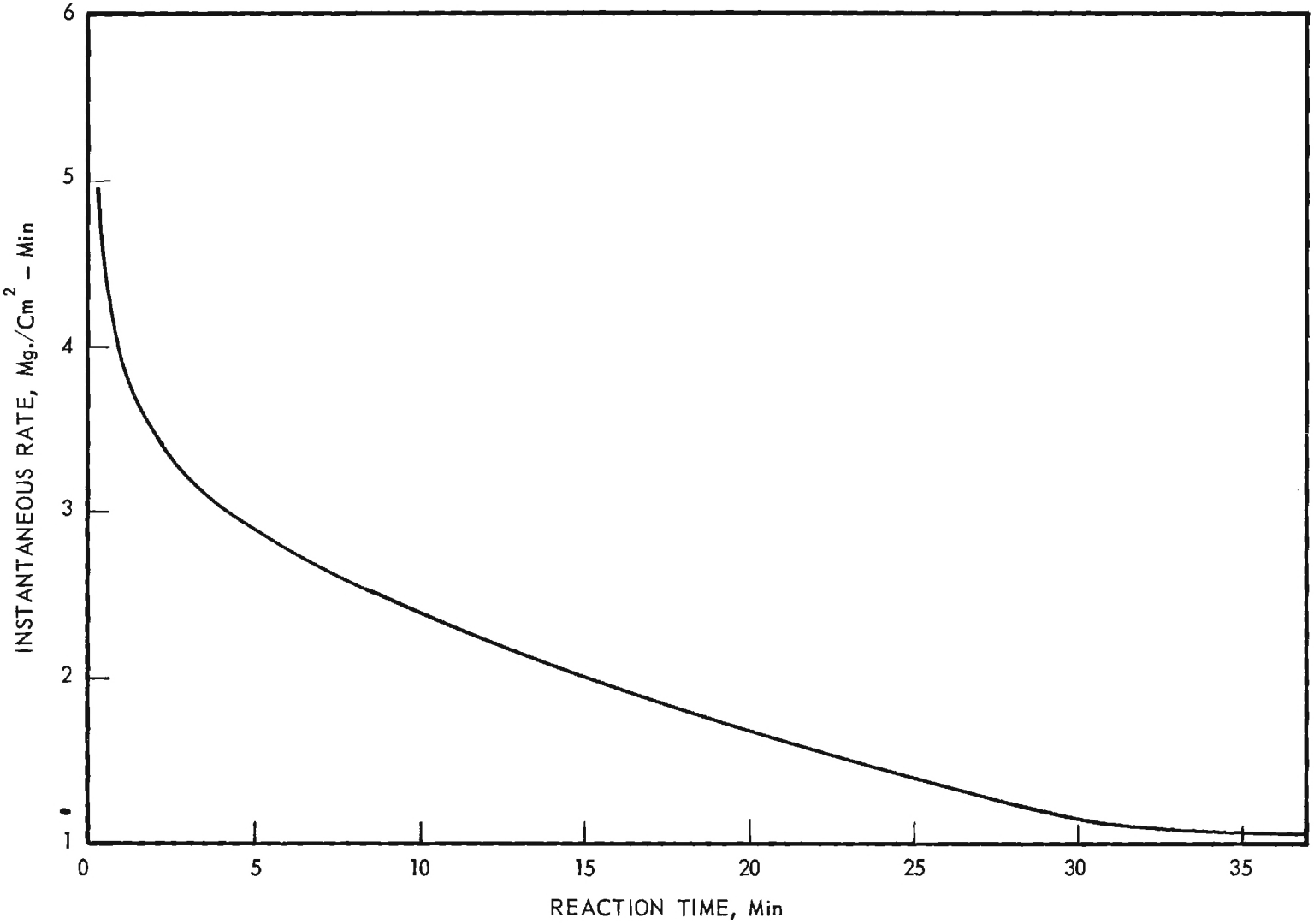

Figure 20. Instantaneous Effect, 0.4 Gm/L Formamidine Disulfide. Flow = 1400 Ml/Min, Temperature = 25°C, Molarity = 2.15.

metallic copper surface. Initially no film is present and the magnitude of the reaction rate is equal to that of the very rapid chemical reaction between copper and ferric chloride with no diffusion process involved. As the cuprous chloride coating increases, the reaction rate sharply decreases; however, the cuprous chloride film is not very adherent and partially falls off. This has actually been observed during the course of experiments on this project. The very rapid film build-up does not allow time for the film to form tightly on the surface. The second decrease in rate occurring after 10 minutes proceeds slowly enough to permit an adherent film to form that apparently approaches an equilibrium thickness after some 35 minutes or more. As the reaction proceeds, the metallic copper is oxidized to form an insoluble cupric chloride. The equilibrium thickness is the film thickness finally attained when the metallic copper oxidation rate just equals the film oxidation rate. It is noted, for no inhibitor present, that the dissolution rate approaches approximately 2.39 milligrams per square centimeter per minute for large reaction times.

Figures 17 and 18, depicting the average and instantaneous rates respectively for 0.20 gram per liter, have several features different from the curves with no inhibitor present. The reaction rate does not decrease as rapidly as in Figure 16 and exhibits no maximum or minimum, but smoothly approaches a limiting value for large reaction times. The apparent asymptote has the value of 1.70 milligrams per square centimeter per minute as compared to 2.39 milligrams per square centimeter per minute for the copper-ferric chloride reaction with no inhibitor present. This supports the observation of a thicker surface film for the inhibited reactions.

Figures 19 and 20 at 0.40 gram per liter formamidine disulfide show the effect of increased inhibitor concentration on the average reaction rate and

instantaneous rate. The average rate, after an initial sharp decrease, decreases almost linearly over the 35 minutes studied. The instantaneous reaction rate is shown to decrease more slowly and approaches an asymptote after 30 minutes. The asymptote value for 0.40 gram is about 1.00 milligrams per square centimeter per minute as compared to 1.70 and 2.39 milligrams per square centimeter per minute for 0.20 and 0.0 gram per liter formamidine disulfide respectively. These values reveal a linear decrease in the asymptotic value of the dissolution rate with increasing inhibitor concentration. However, as noted for Figures 13 and 14, at a reaction time of 12.75 minutes the curve of reaction rate versus inhibitor concentration is definitely not linear. This only shows that the intermediate behavior, before reaching the reaction rate asymptote, is very complex; and a function to explain the role of the inhibitor cannot be given satisfactorily.

C. Effect of Temperature

A series of 15 experiments was conducted to study the temperature effect on the reaction rate at various inhibitor concentrations. These data are presented in Table XII and plotted in Figure 21. Differences between Figures 21 and 13 are quite noticeable. While the increase in flow rate did not displace the positions of the maxima and minima, the increased temperature has shifted their positions. The first minimum still occurs at 0.17 gram per liter; however, the first maximum is at 0.49 gram per liter compared to 0.41 gram per liter for both 25° C series of experiments. The second minimum in Figure 21 is approximated, as insufficient time was available for investigation of this area. The minimum probably is at 0.55 gram per liter as compared to 0.45 gram per liter in the 25° C cases. The second maximum occurs at 0.61 gram per liter, while at 25° C it is at 0.50 gram per liter of formamidine disulfide.

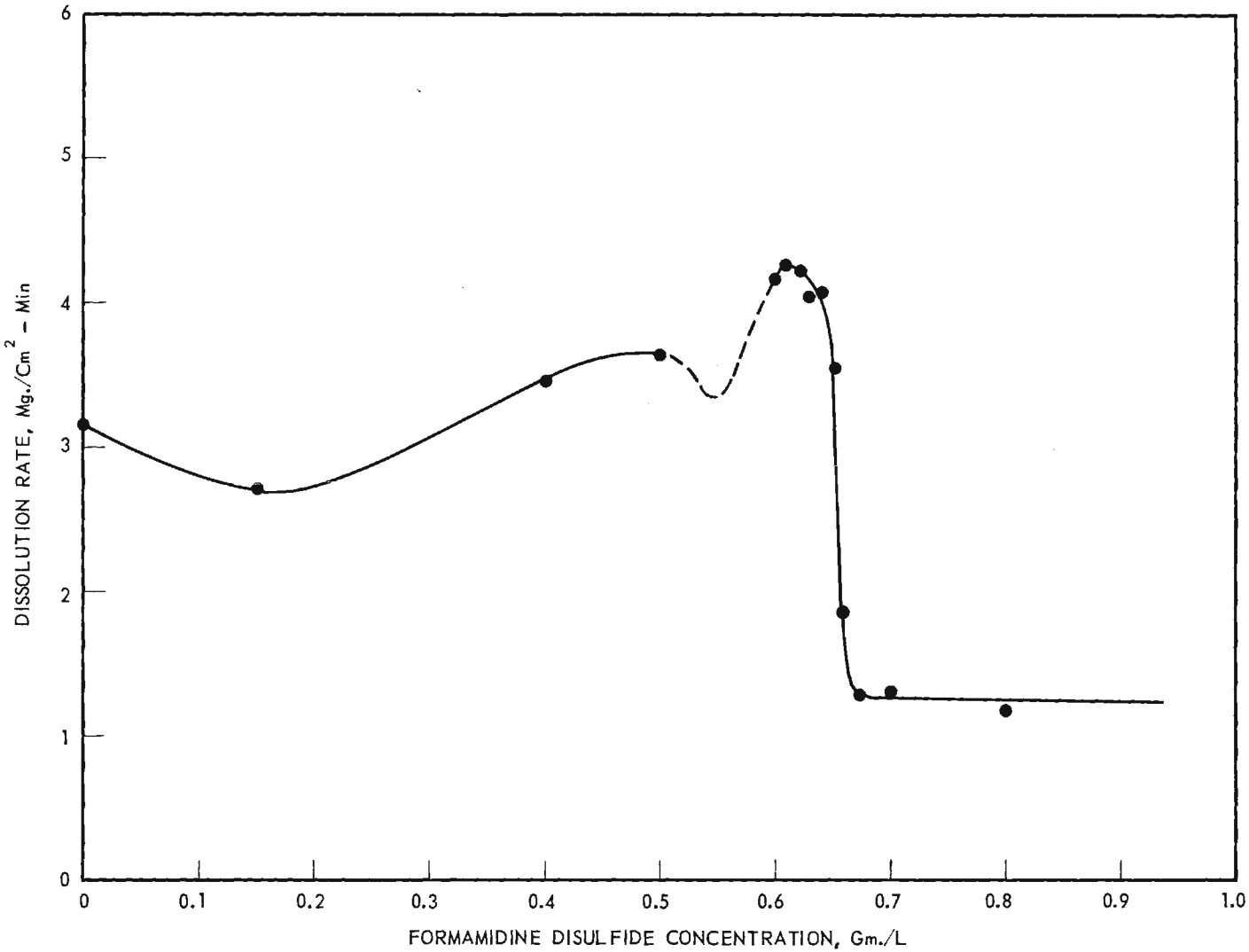

Figure 21. Formamidine Disulfide Effect at 1400 Ml/Min and 30°C. Flow = 1400 Ml/Min, Temperature = 30°C, Reaction Time = 12.75, Molarity = 2.15.

TABLE XII

FORMAMIDINE DISULFIDE INHIBITOR STUDY,
TEMPERATURE EFFECT

Temperature = 30° C, Flow Rate = 1400 Ml/Min
$FeCl_3$ Concentration = 2.15 Moles/L

Reaction Time (Min)	Inhibitor Concentration (Gm/L)	Dissolution Rate (Mg/Cm^2-Min)
12.75	0.00	3.16
12.75	0.15	2.72
12.75	0.40	3.44
12.75	0.50	3.63
12.75	0.60	4.16
12.75	0.61	4.28
12.75	0.62	4.23
12.75	0.63	4.03
12.75	0.64	4.09
12.75	0.65	3.54
12.75	0.66	1.88
12.75	0.675	1.29
12.75	0.70	1.32
12.75	0.80	1.19
12.75	1.00	1.27

The major differences are noted as: (1) A general spreading of the dissolution curve to the right as temperature increases, (2) An increase in reaction rate that can be attributed to the increased temperature and (3) A maximum at 0.61 gram per liter that is considerably greater than the rate with no inhibitor present.

D. Effect of Ethylene Thiourea

It was decided to study another inhibitor, ethylene thiourea, which had been shown (21) to have superior inhibitor characteristics. Twenty-one experiments were conducted to obtain data comparable to those obtained for formamidine disulfide. These data are listed in Table XIII for a temperature of 25° C and

TABLE XIII

ETHYLENE THIOUREA INHIBITOR STUDY

Temperature = 25° C, Flow Rate = 1400 Ml/Min
$FeCl_3$ Concentration = 2.15 Moles/L

Reaction Time (Min)	Inhibitor Concentration (Gm/L)	Dissolution Rate (Mg/Cm^2-Min)
0.50	0.20	4.21
4.00	0.20	2.57
4.00	0.20	2.48
8.00	0.20	2.24
12.75	0.05	2.56
12.75	0.10	2.50
12.75	0.15	2.12
12.75	0.20	2.29
12.75	0.20	2.48
12.75	0.25	2.42
12.75	0.26	1.40
12.75	0.26	2.11
12.75	0.27	2.27
12.75	0.28	1.57
12.75	0.30	1.37
12.75	0.40	1.21
12.75	0.50	1.23
12.75	0.80	1.14
17.00	0.20	2.07
25.00	0.20	2.00
45.00	0.20	1.90

1400 milliliters per minute flow rate. A graph of dissolution rate versus ethylene thiourea concentration (Figure 22) reveals an initial sharp decrease followed by a small constant decrease in rate. Between 0.10 and 0.20 gram per liter the actual shape of the curve is not known. It is probable that it continues with no maximum or minimum; however, one data point at 0.15 gram per liter poses the question of a minimum. The sharp decrease at 0.27 gram per liter followed by the almost constant rate thereafter appears typical for all inhibitor studies made. While the sharp decrease for ethylene thiourea occurs at a lower mass concentration than it does for formamidine disulfide, it can be shown that in both cases the decrease occurs at approximately the same molar concentration of inhibitor. Based on a molecular weight of 102.16 for ethylene thiourea and 223.16 for formamidine disulfide ($C_2H_8N_4S_2Cl_2$), the concentration at the sharp decrease is approximately 2.5×10^{-3} gram moles per liter for both inhibitors at 25° C and a flow rate of 1400 milliliters per minute. This supports the theory of an actual attraction of a chemical nature between the metallic copper surface and the inhibitors.

Time effect studies were also conducted for ethylene thiourea at 0.20 gram per liter, and graphs of the average and instantaneous rates are presented in Figures 23 and 24 respectively. Curves similar to those for formamidine disulfide resulted. The asymptote value for long reaction times has the value 1.92 milligrams per square centimeter per minute. A difference between inhibitors may be seen in that the asymptotic value is approached more rapidly for ethylene thiourea.

V. CONCLUSIONS

Experiments conducted at temperatures of 25°, 35°, and 45° C show the reaction rate to have a second order molarity dependence based on the "F"

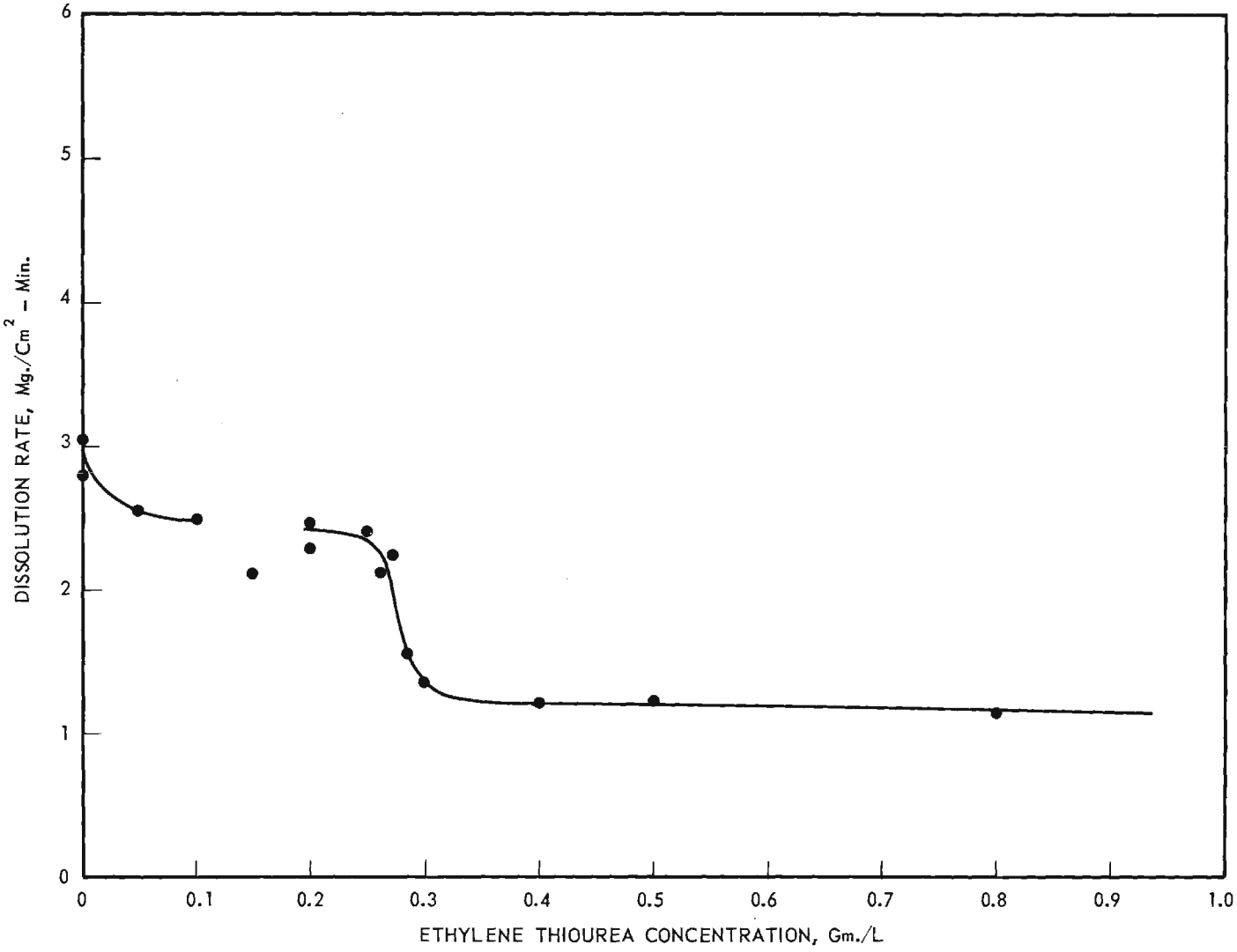

Figure 22. Ethylene Thiourea Effect at 1400 Ml/Min and 25°C.
Flow = 1400 Ml/Min, Temperature = 25°C, Reaction Time = 12.75,
Molarity = 2.15.

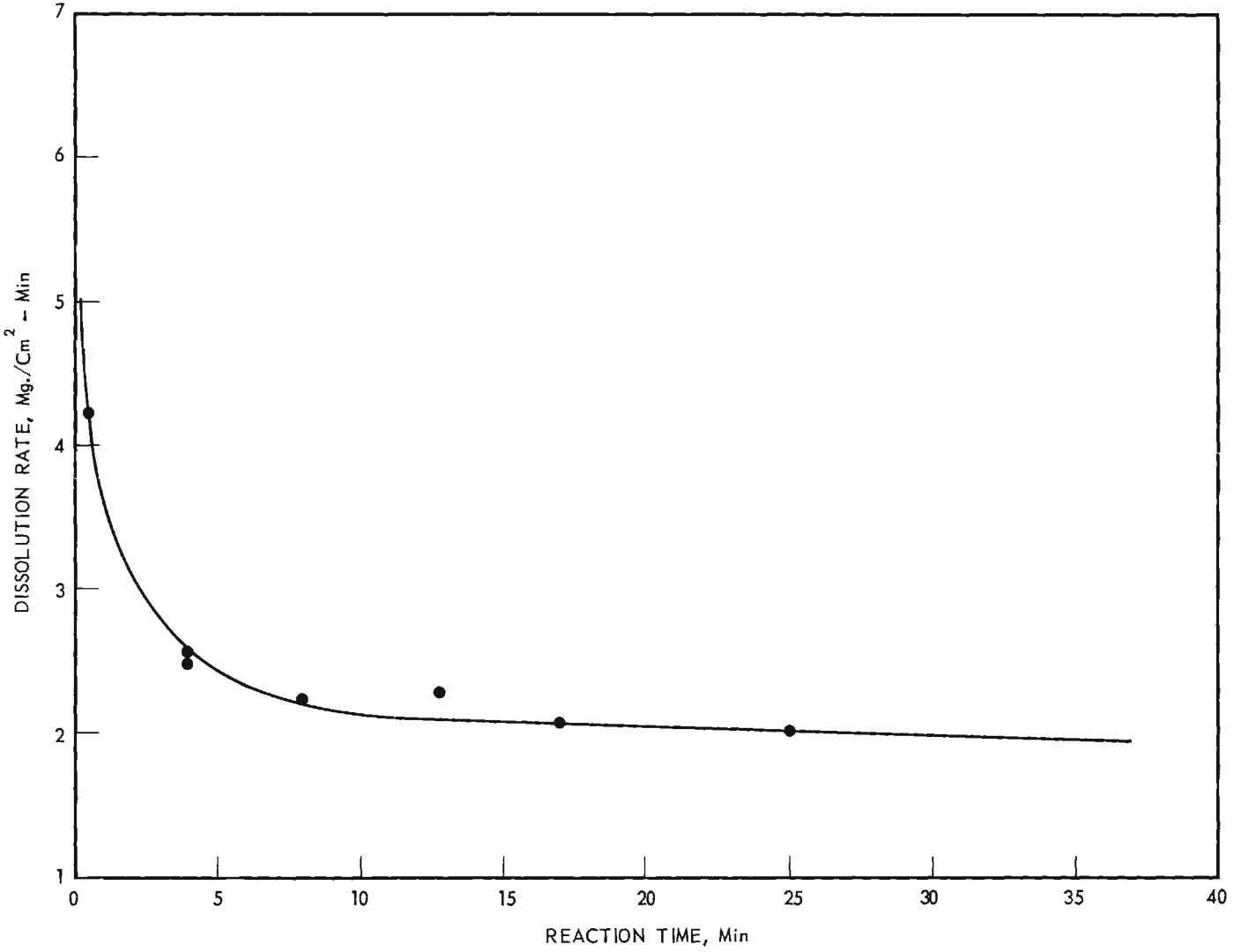

Figure 23. Reaction Time Effect, 0.2 Gm/L Ethylene Thiourea.
Flow = 1400 Ml/Min, Temperature = 25°C, Molarity = 2.15.

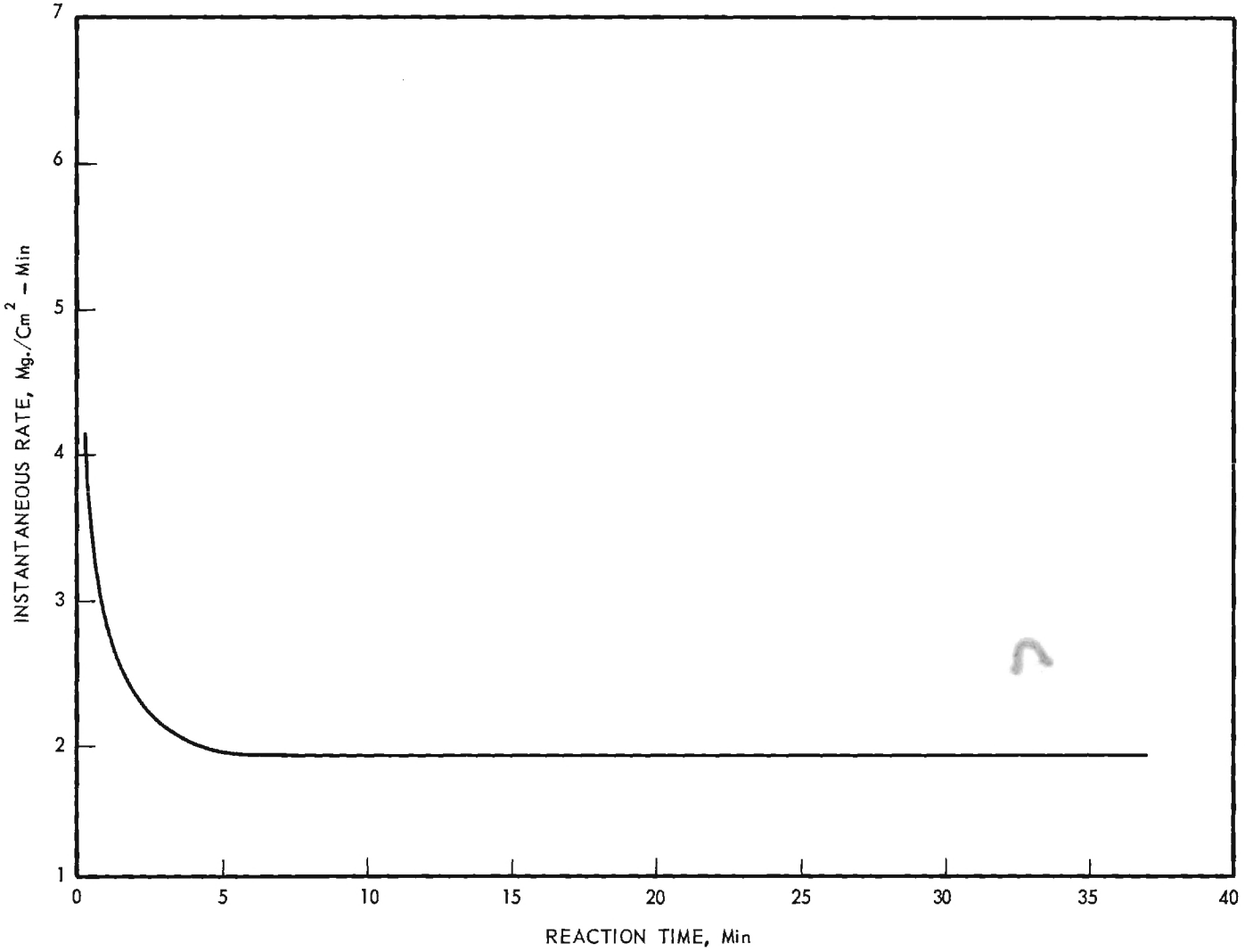

Figure 24. Instantaneous Effect, 0.2 Gm/L Ethylene Thiourea.
Flow = 1400 Ml/Min, Temperature = 25°C, Molarity = 2.15.

goodness of fit test for polynomials. A slight fourth order dependence was noted for 45° C. Inspection of curves of these data show the dissolution rate to increase linearly with increasing molarity up to a concentration of one-molar ferric chloride. Above one molar the rate increases more slowly, reaching a maximum between 2.0 and 2.5 molar and then decreasing with further increase in ferric chloride molarity.

All temperature coefficients varied from 1.04 to 1.57 per 10° C rise over the range studied. An Arrhenius activation energy range from 3810 to 4240 calories per mole was calculated with an average value of 4040 calories per mole.

Flow rate studies show the maximum dissolution to occur at a molarity of 2.15-molar ferric chloride for solution flow rates of 700, 1400, 2100, and 5500 milliliters per minute. The goodness of fit test shows a second order molarity dependency as previously noted for the temperature studies. A linear dependence of the reaction rate on the flow rate was noted and an average value of this increase was calculated to be 4.45×10^{-4} milligrams per square centimeter per milliliter.

The temperature coefficient, the activation energies and the linear flow rate dependence help support the postulate of a diffusion-controlled reaction between copper and ferric chloride. Also, a reaction rate dependence on the sample position adds further proof to this postulate.

Oxygen appears to be a surface poison in the copper-ferric chloride reaction. It is proposed that upon absorption of the oxygen on the metallic copper surface the oxygen reduces the number of active centers available for the copper-ferric chloride reaction.

Viscosity and density data are presented with an accompanying derivation of the actual molarity function which depends on the kinematic viscosity. Based on this equation it is proposed that the order of reactivity, in increasing order, of ferric ions and complexes is: Fe^{+3} and $FeOH^{+2}$, $FeCl_2^+$ and $FeCl^{+2}$. $FeCl_3$ is not believed to be reactive.

Studies of the inhibitors thiourea, ethylene thiourea, and formamidine disulfide revealed similar maximum molar concentrations above which only a constant reaction rate occurred. However, for formamidine disulfide several maxima and minima occurred that were not believed to exist for ethylene thiourea.

The effect of temperature and flow rate on the reaction rate at various concentrations of inhibitors showed that varying the flow rate changed the heights of the maxima and minima but not their position. The increased temperature, however, shifted their position to higher concentration of inhibitors.

VI. PRACTICAL ASPECTS OF THIS RESEARCH

While the study described in this report is a fundamental study of the reaction kinetics and effects of inhibitors on the rate of the subject reaction, it is nevertheless true that both the reaction and the inhibitors included in this study are of prime interest in the photoengraving process. The reaction is the standard one used for the production of copper etchings and the inhibitors are among those developed in recent years for the prevention of undercutting in the "powderless" process for copper.

This process is of tremendous cultural and commercial significance, as it provides one of the most widely used means for transferring ideas, pictures and illustrations to the printed page. In recent years it has acquired additional significance in the field of electronics and, thereby, in national defense, through its use in the production of printed circuits. In this application

copper is the only satisfactory metal, and the "powderless" process is required to provide high quality, dependable circuits.

Still under development is another application of this process, the production of miniature and microminiature electronic components; resistors, condensers, etc. Miniaturization of electronic components is a necessary adjunct to the development of solid state elements; transistors, diodes, etc., and in conjunction with such elements provides highly compact circuits capable of reliable, long-time service at very low energy requirements. Circuits of this kind are essential to satellite and long-range missile communications systems, and are finding many applications in computer circuitry as well as in the more mundane communications systems. Advanced techniques of photoengraving, coupled with the techniques of deposition of thin films of metals and dielectrics, provides a tool of great potential in the area of microminiaturization.

Of immediate practical interest in the selection of an inhibited ferric chloride system for etching copper under a given set of conditions are the following results obtained in this study: 1. Concentration of ferric chloride for maximum reaction rate, 2. Minimum concentration of inhibitor for effective and consistent results, 3. Effect of temperature upon minimum concentration of inhibitor, 4. Time lag in reaching full effect for various inhibitors, and 5. Correlation of effective inhibitor concentration with molecular weight.

With the photoengraving process becoming of increasing importance in national defense and commerce, there is much need for further research of the type reported here. Two major stepping stones to further research are provided in this report. First, a close relationship is observed between the results obtained here and results obtained in commerical studies of inhibitors for sidewall protection in copper etching; consequently, the techniques developed for this study are readily

adaptable to further studies with full assurance that the results obtained will be immediately applicable to the design of new inhibited ferric chloride systems. Second, some of the fundamental characteristics of the inhibiting action are revealed in this research. This provides a basis for the selection of compounds for further study as inhibitors and defines more clearly than ever before the specific objectives of this highly specialized application of chemical inhibition.

Respectfully submitted:

W. H. Burrows
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

for J. E. Boyd, Director
Engineering Experiment Station

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